Electrochemical Behaviour of an Iron Substituted Polyoxometalate Incorporated in an Electropolymerized Film

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Hybrid inorganic/organic films composed of an polyoxometalate (POM) (iron(III)-trisubstituted Keggin polyoxomolybdates, PFe_3Mo_9) and a non-conducting polymer [(poly(ortho-phenylenediamine)) or a conducting polymer (poly(1,8-diaminonaphtalene)) were synthesized by electropolymerization from aqueous solution on the surface of a graphite electrodes. Cyclic voltammetry gave evidence of a redox behaviour of the PFe_3Mo_9, irrespective of the type of polymer used for POM immobilization into the composite matrix.

Keywords: polyoxometalate, electropolymerization, hydrogen peroxide, glucose

Polyoxometalates (POMs) are a class of metal oxides that represent a various range of molecular clusters, acting as a set of convenient building blocks that can be utilized in the creation of new dynamic structures that can vary in size from the nano- to the micrometer scale [1]. Among their interesting and important physical and chemical properties, the ability to undergo reversible multi-electron redox processes, giving rise to mixed-valence species, recommending them as very attractive materials for use in the preparation of chemically modified electrodes (CME) and in electrocatalysis [2]. The traditional CMEs with POMs can be achieved by many methods: (i) surface modification based on electrostatic interactions, including electrochemical deposition, adsorption, entrapment into polymeric matrices, layer-by layer self-assembly methods; (ii) sol–gel technique; and (iii) other strategies [2,3].

During the last several years, there has been observed an increasing interest in using polymer films due to the expectation of their application in different fields, such as [4]: electroanalysis, energy storage, electrocatalysis, biosensing, corrosion protection [2], sensors and electronic devices (e.g. sophisticated electronic measuring devices such as artificial sensor in the goal of mimicking natural sense organs, molecular electronics [2, 5]), electrochromic displays (e.g. displays and light emitting diodes [2]). Thus, in the field of sensors research, higher selectivity and sensitivity have been acquired by replacing classical sensor materials (e.g. semiconductors, semiconducting metal oxides, solid electrolytes, ionic membranes, and organic semiconductors) with polymers involving nanotechnology and exploiting either the intrinsic or extrinsic functions of polymers [5]. Among these, intrinsically conducting polymers, also known as "synthetic metals" are polymers with a highly π-conjugated polymeric chain [6], which have attracted much attention as advances materials, due (i) to the high conductivities of their oxidized forms and their ability to reversibly switch between conducting (oxidized) and insulating (reduced) states [4], and (ii) to the potential applications [7]. As known, electropolymerization supposes new covalent bonds formation by oxidation or reduction of certain organic monomer precursors, distinguishing this process from simple electrodeposition [8]. For chemically modified electrode development, the electropolymerization [4] is the most convenient, advantageous and powerful way to obtain films of conducting (e.g., poly(aniline)s, poly(pyrrole)s, poly (thiophene)s and their derivatives, poly (diaminonaphthalene)s) [2,5-7,9-11] or non-conducting (e.g., phenol and its derivatives, phenylenediamines [4], and overoxidized or electroinactive polypyrrole) [12] polymers.

Thus, the synthesis of new hybrid materials with combined properties derived from its organic and inorganic compounds could be realized from a positive charged polymer doped with anionic species, such as redox-active Keggin-type polyoxometalates, in view to be neutralized and to maintain its electroneutrality [2,5,13]. The new material has higher density and conductivity than the polymer alone. When at its interface an oxidation or a reduction reaction occurs, the presence of active ionic species immobilized into the polymeric matrix force the cations (instead of the anions), present in the bulk medium to diffuse through the polymer structure. In addition, polyoxometalates anions have high volume and charge, so their diffusion coefficient is low, and their exchange with anions present in the solution is avoided [13]. As consequence, the production of new devices using polyoxometalates, that maintain and enhance their beneficial properties, is of great interest.

In this context, it is of interest to compare the electrochemical behaviour of a hybrid inorganic/organic matrix, composed from an iron(III)-trisubstituted Keggin polyoxotungstates (PFe_3Mo_9) [14] and a non-conducting [poly(*ortho*-phenylenediamine), poly (1,2-DAB)] or a conducting polymer [poly(1,8-diaminonaphtalene), poly(1,8-DAN)] [15]. The composite matrix was immobilized by electropolymerization on the surface of a graphite electrode and characterized by cyclic voltammetry, in view to obtain the electrochemical parameters of the POM and its electrocatalytic properties towards H_2O_2 and glucose detection.

Experimental part

Reagents

The trilacunary Keggin type $Na_3H_3[A\alpha\text{-}PFe^{III}_3(H_2O)_3Mo_9O_{37}]$. 14 H_2O (PFe_3Mo_9) polyoxometalate was prepared and fully characterized, by a previously published procedure [14].

The *o*-phenylenediamine (1,2-diaminobenzene, 1,2-DAB) and 1,8-diaminonaphthalene (1,8-DAN) monomers were purchased from Fluka Buchs, Switzerland and

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hydrogen peroxide (30% w/v solution) was from J. T. Baker. A 0.4 M Na_2SO_4 (*p*H 2.4) (Switzerland) and 0.2 M NaCl (Carlo Erba, Italy) solutions were used as the supporting electrolytes. A phosphate buffer solution (*p*H 6.5 - 7) was prepared from a 0.1 M KH_2PO_4 and 0.1 M K_2HPO_4 (Switzerland) solution by adjusting the *p*H with H_3PO_4.

Glucose oxidase (GOx) (E.C. 1.1.3.1, type VII, purified from *Aspergillus Niger*; Sigma Chemical Co, St. Louis, Mo, U.S.A), D(+) glucose (Carlo Erba, Italy), bovine serum albumine (BSA) (Fluka Buchs, Switzerland) and 25 % aqueous solution of glutharaldehyde (GA) (U.S.A) were used for assembling the biosensor.

All chemicals were of analytical grade and were used without further purification. The solutions were prepared with distilled water. For *p*H adjustments, pellets of NaOH, H_2SO_4 or HCl solution (Italy) have been used. The buffer solutions were kept refrigerated to minimize bacterial growth. All stock solutions were prepared daily.

Apparatus

Voltammetric measurements and electropolymerization of 1,2-DAB or 1,8-DAN monomers were carried out using a computer controlled Autolab-PGSTAT 10 voltammetric analyzer (Netherlands). Batch amperometric measurements were performed under stirring conditions, using a potentiostat AMEL 559 (Italy) coupled to an X-t recorder (LKB Bromma 2210 Recorder, Italy).

All measurements were done using a conventional single-compartment three electrode system consisting of a platinum wire counter electrode, an Ag/AgCl,KCl_{sat} reference electrode and a graphite (3 mm diameter) (Germany) working electrode. All experiments were done at room temperature.

A combined glass electrode (Hanna Instruments HI 1230) connected to a pH meter (model *p*H 20) was used for the *p*H measurements.

Preparation of G/PFe$_3$Mo$_9$-poly(monomer) modified electrode

Prior modification, the graphite electrode was conditioned by a cleaning/polishing procedure, using diamond paper for cleaning and 1.0, 0.3, 0.05 μm α-Al_2O_3 paste (Buehler, Evanston, IL, USA) for polishing, and followed by a sonication in distilled water to remove any residual alumina.

On G/PFe_3Mo_9-poly(1,8-DAN) modified electrodes the electropolymerized film was grown from an unstirred deaerated (15 min. with nitrogen) solution containing 5 mM 1,8-DAN and 1 mM PFe_3Mo_9 in 0.2 M NaCl (*p*H 1), by cycling the potential between -0.15 and 1.3 V *vs.* Ag/AgCl, KCl_{sat}.

In the case of G/PFe_3Mo_9-poly(1,2-DAB) modified electrodes the electropolymerized film was grown from an unstirred deaerated solution containing 0.05 M 1,2-DAB and 1 mM PFe_3Mo_9 in 0.5 M K_2SO_4 (*p*H 2.5).

After preparation, the G/PFe_3Mo_9-poly(monomer) modified electrodes were thoroughly rinsed with distilled water and stored at +4°C in dry state, when not in use.

Preparation of G/PFe$_3$Mo$_9$-poly(monomer)/GOx biosensor

A G/PFe_3Mo_9-poly(1,8-DAN)/GOx glucose biosensor was prepared using a 200 μL of a phosphate buffer solution (*p*H 6.5) containing 2 mg BSA, 500 U GOx and 2 μL of 1% glutaraldehyde solution. A volume of 4 μL of the resulting solution were carefully dropped on the tip of the G/PFe_3Mo_9-poly(1,8-DAN) modified working electrode surface (avoiding air bubble formation) and air-dried at room temperature. When not in use the enzyme electrodes were stored at +4°C, in dry state.

Electrochemical measurements

The preparation and the characterization of a modified G/PFe_3Mo_9-poly(monomer) electrodes were carried out by cyclic voltammetry, performed at different potential scan rates, using as supporting electrolyte a 0.2 M NaCl solution (*p*H 1.1) and a 0.4 M Na_2SO_4 (*p*H 2.4) solution, for 1,2-DAB or 1,8-DAN monomer used, respectively.

The amperometric responses of the G/PFe_3Mo_9-poly(monomer) modified electrodes to H_2O_2 and glucose, respectively, were investigated in a stirred, air-saturated 0.1 M phosphate buffer solution (*p*H 6.5), by applying a constant potential of -0.1 V *vs.* Ag/AgCl, KCl_{sat} (for G/PFe_3Mo_9-poly(1,2-DAB) electrode) and -0.04 V *vs.* Ag/AgCl, KCl_{sat} (for G/PFe_3Mo_9-poly(1,8-DAN) electrode). The background current was allowed to decay to a steady value, before aliquots of H_2O_2 or glucose standard solutions were added and the steady-state reduction currents were recorded.

Results and discussions

Electrochemical behaviour of G/PFe$_3$Mo$_9$-poly(monomer) modified graphite electrode

In the last years, the electrochemical polymerization of 1,2-DAB and 1,8-DAN was used to form a polymer matrix for immobilizing different substances like mediators and enzymes, in view to obtain chemically modified electrodes having electrocatalytic properties or biosensors. Cyclic voltammetric technique applied to a graphite electrode placed into a solution containing 10^{-3} M PFe_3Mo_9 dissolved in an adequate electrolyte and a monomer 1,2-DAB ($5\ 10^{-2}$ M) or 1,8-DAN ($5\ 10^{-3}$ M) lead to obtain a composite matrix of a modified electrode (figure 1A and 1B). For keeping a good electrochemical behaviour of PFe_3Mo_9 and in order to increase the monomer solubility (e.g. 1,8-DAN), low *p*H values of electrolyte solution have to be used.

It is well known that the oxidation peak in the poly(1,2-DAB) electropolymerization, placed at about +0.28 V *vs.* SCE (on mild steel electrode in oxalic acidic media) corresponds to removing one electron from nitrogen atom

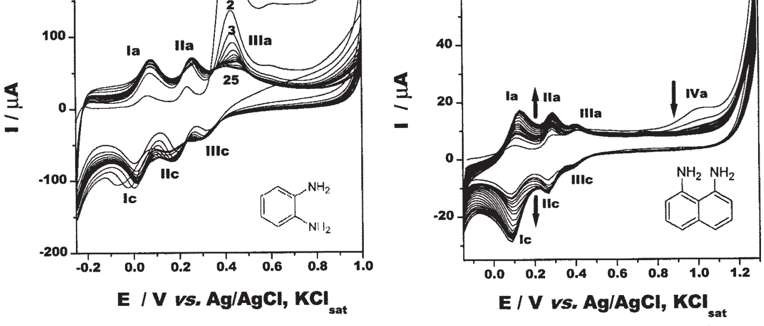

Fig. 1. Preparation of G/PFe_3Mo_9-poly(1,2-DAB) (A) and G/PFe_3Mo_9-poly(1,8-DAN) (B) modified electrode by electropolymerisation. Experimental conditions: starting potential, -0.25 (A) or -0.2 V (B) (*vs.* Ag/AgCl, KCl_{sat}); potential scan rate, 50 mV/s (A) or 10 mV/s (B); electropolymerization solution, 0.05 M 1,2-DAB + 10^{-3} M PFe_3Mo_9 + 0.5 M K_2SO_4 (pH 2.5) (A), 5 mM 1,8-DAN + 10^{-3} M PFe_3Mo_9 + 0.2 M NaCl (pH 1.1) (B), deaerated with nitrogen; 25 cycles.

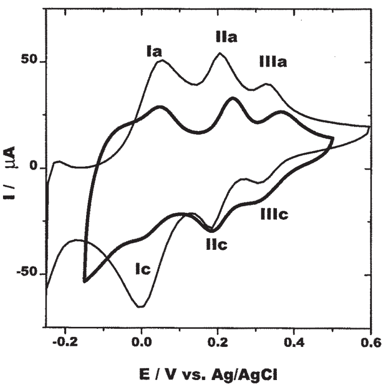

Fig. 2. Voltammetric response of the G/PFe_3Mo_9-poly(1,2-DAB) (thick line) and G/PFe_3Mo_9-poly(1,8-DAN) (thin line) modified graphite electrode prepared as in figure 1. Experimental conditions: starting potential, -0.25 V (thin line) or -0.15 V (thick line) *vs.* Ag/AgCl, KCl_{sat}; potential scan rate, 50 mV/s; supporting electrolyte, 0.4 M Na_2SO_4 (pH 2.5).

Table 1
INFLUENCE OF THE POTENTIAL SCAN RATE ON THE VOLTAMMETRIC RESPONSE OF G/PFE_3MO_9-POLY(1,2-DAB) AND G/PFE_3MO_9-POLY(1,8-DAN) MODIFIED ELECTRODES
EXPERIMENTAL CONDITIONS: SEE FIGURE 2.

Electrode	Slope of the log I *vs.* log v dependence Correlation coefficient (R) / no. of experimental points (n)					
	Ia	**Ic**	**IIa**	**IIc**	**IIIa**	**IIIc**
G/PFe_3Mo_9-poly(1,2-DAB)	0.88 ± 0.02 0.9984 / 8	0.71 ± 0.05 0.9834 / 8	0.79 ± 0.03 0.9946 / 8	0.79 ±0.03 0.9969 / 8	0.66 ± 0.02 0.9980 / 8	0.97 ± 0.02 0.9985 / 8
G/PFe_3Mo_9-poly(1,8-DAN)	0.58 ± 0.02 0.9967 / 9	0.59 ± 0.01 0.9985 / 9	0.80 ± 0.01 0.9990 / 9	0.75 ± 0.01 0.9998 / 9	0.84 ± 0.01 0.9998 / 9	0.97 ± 0.02 0.9989 / 9

of one of the amino groups to give radical cation and the corresponding cathodic peak observed around +0.2 V *vs.* SCE, could be attributed to the reduction of this obtained radical cation [16]. In our case, the high current intensity of IIIa oxidation peak recorded during G/PFe_3Mo_9-poly(1,2-DAB) electrode preparation is the effect of the superposition of the electrochemical behavior of the PFe_3Mo_9 and of 1,2-DAB (fig. 1A). Also, from figures 1A and 1B it is easily to observe that the growth of the polymer film, confirmed by the gradual decrease of the IIIa and IVa peak current intensities, respectively (assigned to the monomer), is followed by the PFe_3Mo_9 accumulation inside the polymer matrix [17].

For both electrode cases, the augmentation of PFe_3Mo_9 content inside the polymer matrix is confirmed by the gradually increase of I, II and III peak current intensities. Irrespective of the polymer type, it is plausible the hypothesis that a hybrid inorganic/organic architecture composed by $(PFe_3Mo_9\text{-polymer})_n$ supramolecular structures are obtained *via* a successive deposition of a bi-layer structure, favored by the electrostatic interactions existing between the positive charges (polymeric matrix at low pH value) and negative charges (PFe_3Mo_9 polyanion) presented at the electrode surface [18].

As expected, both the G/PFe_3Mo_9-poly(1,2-DAB) and G/PFe_3Mo_9-poly(1,8-DAN) electrode exhibited a voltammetric response materialized in three good shaped peak pairs corresponding to PFe_3Mo_9 redox behaviour (fig. 2) placed at similar potentials and having quasi-similar current intensities values. Also, despite the fact that the solution of 1,2-DAB for electropolymerization was 10 times more concentrated than the 1,8-DAN solution, at the similar scan rate, the intensities of the corresponding PFe_3Mo_9 peaks recorded at G/PFe_3Mo_9-poly(1,2-DAB) modified electrode are smaller than at the G/PFe_3Mo_9-poly(1,8-DAN) modified electrode. This fact prove that the immobilization of PFe_3Mo_9 redox couple into a non-conducting or conducting polymer matrix is controlled by the strength of the interactions between the negative and positive charges, represented by the PFe_3Mo_9 anions and the cationic sites of the polymers, respectively.

The peak potential splitting (calculated as $\Delta E_p = E_{p,a} - E_{p,c}$) was found different of zero for all I to III pair of peaks at G/PFe_3Mo_9-poly(1,2-DAB) (I: 40 mV; II: 53 mV; III: 53 mV), and at G/ PFe_3Mo_9-poly(1,8-DAN) (I: 45 mV; II: 20 mV; III 20 mV) modified electrodes (both at scan rate of 50 mV/s, *p*H 2.5), indicating the existence of a quasi-reversible electron transfer process, because of interactions existing between the surface confined redox couples [19,20]. Also, the formal potentials, estimated as arithmetic mean of the anodic and cathodic peak potentials for the three pairs of peaks, are not significantly different for G/PFe_3Mo_9-poly(1,2-DAB) (I: 0.029 V, II: 0.213 V, III: 0.346 V) and for G/PFe_3Mo_9-poly(1,8-DAN) (I: 0.023 V, II: 0.195 V, III: 0.330 V) [15], respectively.

For I-III peak pairs the charge transfers processes are described by the following reactions [14]:

Ia/Ic

$$[PFe^{III}_3(H_2O)_3Mo^{VI}_9O_{37}]^{6-} + 2H^+ + 2e^- \rightarrow [H_2PFe^{III}_3(H_2O)_3Mo^{VI}_7Mo^{V}_2O_{37}]^{6-}$$

IIa/IIc

$$[H_2PFe^{III}_3(H_2O)_3Mo^{VI}_7Mo^{V}_2O_{37}]^{6-} + H^+ + e^- \rightarrow [H_3PFe^{III}_2Fe^{II}(H_2O)_3Mo^{VI}_7Mo^{V}_2O_{37}]^{6-}$$

IIIa/IIIc

$$[H_3PFe^{III}_2Fe^{II}(H_2O)_3Mo^{VI}_7Mo^{V}_2O_{37}]^{6-} + H^+ + 2e^- \rightarrow [H_4PFe^{II}_3(H_2O)_3Mo^{VI}_7Mo^{V}_2O_{37}]^{7-}$$

The influence of the potential scan rate on the peak current intensities of the modified electrodes was investigated in the range of 25-500 mV/s (for G/PFe_3Mo_9-poly(1,2-DAB)) or 5-500 mV/s (for G/PFe_3Mo_9-poly(1,8-DAN)), respectively. The corresponding slope values of the log I *vs.* log v dependence presented in table 1 confirm that irrespective the investigated modified electrodes or peak pairs, a deviation from the theoretical value for the rate exponent (value 1) of a surface confined redox couple, is obtained. Only, the Ia/Ic peak of G/PFe_3Mo_9-poly(1,8-DAN) modified electrode showed an exception of the scan rate dependence, pointing rather that the redox process is under diffusion control. Also, in this context, the plot of cathodic and anodic peak currents for the both studied modified electrodes show a good proportionality to the scan rate, with 0.9834 < R < 0.9998 (fig. 3).

G/PFe_3Mo_9-poly(monomer) as amperometric sensor for H_2O_2

Under stirring conditions amperometric calibrations for H_2O_2 were recorded at an applied potential of -0.1 V *vs.* Ag/

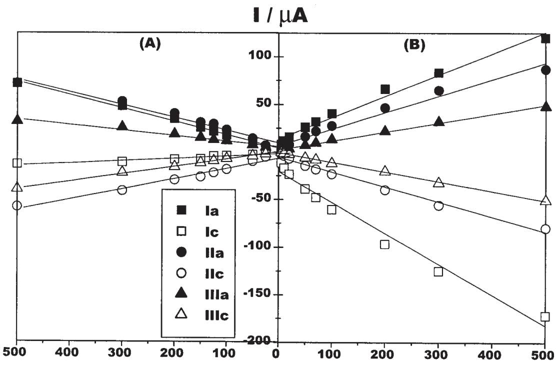

Fig. 3. Influence of the potential scan rate on the voltammetric response of G/PFe$_3$Mo$_9$-poly(1,2-DAB) (A) and G/PFe$_3$Mo$_9$-poly(1,8-DAN) (B) modified electrode. Experimental conditions: see figure 2.

AgCl, KCl$_{sat}$ (for G/PFe$_3$Mo$_9$-poly(1,2-DAB)) and of -0.04 V *vs*. Ag/AgCl, KCl$_{sat}$ (for G/PFe$_3$Mo$_9$-poly(1,8-DAN)) modified electrodes (fig .4). The obtained calibration curves showed a linear range up to 15 mM and 50 mM, with a sensitivity of 2.97 ± 0.33 mA/M and 0.11 ± 0.003 mA/M for G/PFe$_3$Mo$_9$-poly(1,2-DAB) and G/PFe$_3$Mo$_9$-poly(1,8-DAN) modified electrodes, respectively. For both modified electrodes, the time required to reach 95% of the maximum steady-state current ($t_{95\%}$) was less than 1 min. and the detection limit of ~2 mM H_2O_2 (signal/noise ratio of 3).

G/PFe$_3$Mo$_9$-poly(monomer)/GOx as amperometric sensor for glucose

For preparing a G/PFe$_3$Mo$_9$-poly(1,8-DAN)/GOx biosensor the enzyme immobilization was performed by cross-linking in glutaraldehyde (GA) and bovine serum albumin (BSA) matrix, as a separately step, on the already obtained G/PFe$_3$Mo$_9$-poly(1,8-DAN) modified electrode. Probably due to the formation of some covalent bonds between GOx and the -NH$_2$ groups existing in the poly(1,8-DAN), the biosensor shows a good contact between the successively deposited layer on the electrode surface [7].

At low glucose concentrations, as seen in figure 5A, with the increasing of the glucose concentrations, the amperometric response increased linearly in the range from 2.5 and 20 mM (equation: I / nA) = 0.979 + 0.835 [glucose / mM]; R = 0.999, n = 8), domain which include the usual blood glucose concentration for biomedical applications (i.e., 2.2 - 22 mM [21]). The detection limit was found 1.2 mM of glucose, for a signal to noise ratio of 3 [22]. Independent on the substrate concentration, the response time of biosensor was less than 40 s.

At high glucose concentrations the biosensor response follows a typical hyperbolic Michaelis–Menten kinetic mechanism. The apparent Michaelis Menten constant (K_m = 24.5 ± 5.8 mM) and the maximum current intensity (I_{max} = 34.8 ± 4 nA) were calculated according to Hanes-Woolf linearization equation (R = 0.986, n = 12) (fig. 5B) [23]. The K_m constant, which is a reflection of the enzymatic affinity, has a value close to than of the free GOx (27 mM) [24], proving that the used immobilization technique preserves the enzymatic activity of GOx and the proposed electrode exhibits a sufficient higher affinity to glucose. The overall biosensor sensitivity was calculated as I_{max}/K_m ratio, obtaining a value of 20.1 ± 2.4 µA M^{-1} cm^{-2}, which is similar to those reported in the literature for other much friendly immobilization matrix (e.g., 25 µA M^{-1} cm^{-2} for GC/MWNTs-ferrocene-chitosan-GOx [25]. Also, the relative low value of the biosensor sensitivity (in comparison with values of 0.36 -0.81 mA M^{-1} cm^{-2} [26]) could be due to the hindered diffusion of glucose and/or the corresponding H_2O_2, as well as, to the loss of the enzyme activity during the immobilization step.

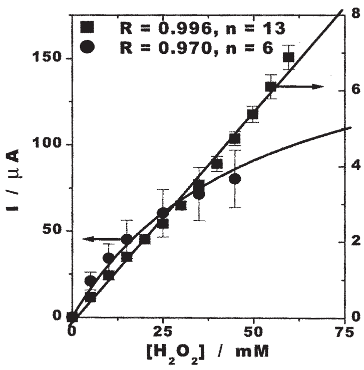

Fig. 4. Amperometric calibration plot for H_2O_2 at G/PFe$_3$Mo$_9$-poly(1,2-DAB) (●) and G/PFe$_3$Mo$_9$-poly(1,8-DAN) (■) modified electrode. Experimental conditions: applied potential, -0.1 V *vs*. Ag/AgCl, KCl$_{sat}$ (●), -0.04 V *vs*. Ag/AgCl, KCl$_{sat}$ (■); supporting electrolyte, phosphate buffer solution (*p*H 7) (●), (pH 6.5) (■); stirred aerated solution.

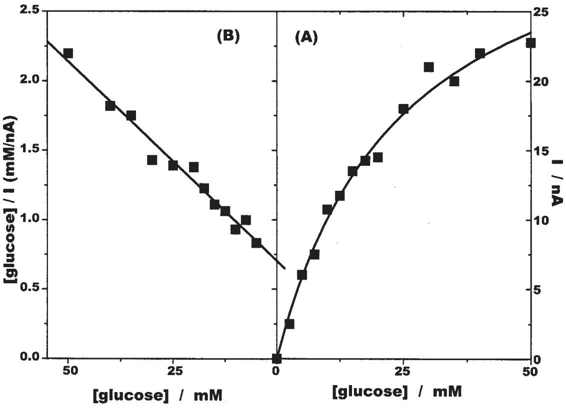

Fig. 5. Amperometric calibration plot for glucose at G/PFe$_3$Mo$_9$-poly(1,8-DAN) bioelectrode (A) and the corresponding Hanes-Woolf linearization (B). Experimental conditions: applied potential, -0.04 V *vs*. Ag/AgCl. KCl$_{sat}$; supporting electrolyte, phosphate buffer (pH 6.5), stirred aerated solution.

Conclusions

In this paper, it was described a promising H_2O_2/glucose sensor/biosensor based on a hybrid inorganic/organic composite matrix performed from a new PFe$_3$Mo$_9$ Keggin-type polyoxometalate and a conducting/non-conducting polymer. Irrespective of the polymer type, the preparation of the G/PFe$_3$Mo$_9$-poly(monomer) modified electrode was probably favoured by the electrostatic interactions existing between the positive charges (electropolymerized matrix of poly (1,2-DAB) or poly(1,8-DAN) at low *p*H value) and negative charges (PFe$_3$Mo$_9$ polyanion) presented at the electrode surface.

Also, the synergy effect of the new iron substituted Keggin-type polyoxometalate and the electropolymerized layer into the hybrid inorganic/organic composite matrix, not only offer an adequate boundary for enzyme matrix, but also establishes/enhances the efficient electronic communication between GOx and the electrode surface resulting in a sensitive amperometric sensor for glucose.

The proposed sensor/biosensor can be operated at a low potential, and under specific conditions exhibits fast amperometric response, excellent wide linear relationships, good sensitivity and a low detection limit for

H_2O_2 or glucose, opening promising perspectives for applications in the field of biosensor and bioelectronic devices.

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