Journal of Applied Electrochemistry (2007) 37:261–267
DOI 10.1007/s10800-006-9251-7

Electrochemical behavior of carbon paste electrodes modified with methylene green immobilized on two different X type zeolites

DELIA GLIGOR, LIANA M. MURESAN*, ANCA DUMITRU and I.C. POPESCU
Department of Physical Chemistry, "Babes-Bolyai" University, Str. Arany Janos, no. 11, RO-400028, Cluj-Napoca, Romania
*(*author for correspondence, tel.: + 40-264-595872, fax: + 40-264-590818, e-mail: limur@chem.ubbcluj.ro)*

Received 20 June 2006; accepted in revised form 19 September 2006

Key words: carbon paste electrode, H_2O_2 electrocatalytic reduction, methylene green, zeolite

Abstract

Two new modified carbon paste electrodes (CPEs) based on two different X type zeolites, a natural zeolitic volcanic tuff (NZ) and a NaX type synthetic zeolite (SZ), modified with methylene green (MG) were developed. Cyclic voltammetry measurements revealed a reasonably fast electron transfer rate and a good stability for both investigated electrodes. The observed differences between the electrochemical behavior of MG-NZ-CPEs and MG-SZ-CPEs (the effect of pH on the formal standard potential, the magnitude of the rate constants for heterogeneous electron transfer and electrode response decay) were explained in terms of zeolites structure. The modified electrodes showed moderate electrocatalytic effect towards H_2O_2 reduction and a relatively low limit of detection (0.5 mM for MG-NZ-CPEs).

1. Introduction

Zeolite modified electrodes (ZMEs) have drawn considerable attention of electrochemists during the past 10 years [1, 2]. The aluminosilicate zeolites, when incorporated into an electrochemical interphase, offer a number of chemical, physical and structural characteristics of high interest in the design of electroanalytical systems: shape, size and charge selectivities, physical and chemical stabilities, high ion-exchange capacity and hydrophilic character [2–5]. These characteristics are very useful in using zeolites as matrix for immobilization of species able to mediate the electron transfer processes for amperometric detection of H_2O_2 [6, 7] and NADH [8]. Therefore, the use of zeolites allows the immobilization of large amounts of efficient mediators with significant solubility in specific experimental conditions. This is essentially the case of redox dyes, used to obtain amperometric sensors with high sensitivity and good stability [9].

Methylene green is a water soluble cationic redox dye, with its formal potential close to the optimal potential domain for amperometric detection [10]. For this reason, it was immobilized on various electrode materials [10–13] or adsorbents [14–17], for the detection of various species of biomedical and biological interest such as NADH [11, 12, 16, 18] and H_2O_2 [6, 13–15]. The ability of a Y type zeolite, entrapped in a polystyrene film, to co-immobilize methylene green and horseradish peroxidase onto glassy carbon electrodes for the construction of H_2O_2 reagentless amperometric biosensors was reported [6]. The authors underlined the importance of the simultaneous presence of micro- and mesopores for the operational stability of the sensor.

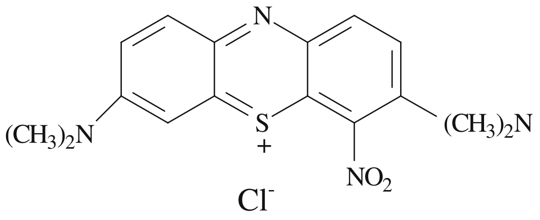
In this context, two new ZMEs based on carbon paste, incorporating methylene green (MG), adsorbed on two different X type zeolites (natural zeolitic volcanic tuff and NaX type synthetic zeolite), were prepared and electrochemically characterized for H_2O_2 detection. In this way, the well-known advantages of carbon paste as entrapping matrix (low background current, wide potential window, versatility etc. [19]) were exploited to immobilize two different X type zeolites, described to have a higher ion-exchange capacity than Y type zeolites [1].

A comparative study, using cyclic voltammetry measurements (CV), performed under different experimental conditions (supporting electrolyte pH and potential scan rate), was carried out in order to investigate the electrochemical behavior of MG adsorbed on the two different zeolites. The kinetic parameters for the heterogeneous electron transfer at MG–zeolite modified CPEs (the rate constant and the transfer coefficient) were estimated using Laviron's treatment [20]. All observed differences were used to put on evidence the influence of the zeolites structure on the MG redox response. Finally, the modified electrodes were examined for their electrocatalytic activity toward H_2O_2 reduction.

2. Experimental

2.1. *Reagents*

Methylene green (see Scheme 1) was purchased from Janssen Chimica (Beerse, Belgium), graphite powder and paraffin oil from Fluka (Buchs, Switzerland).



Scheme 1. Structure of Methylene green (MG).

The zeolitic volcanic tuff (natural X type mesoporous clinoptilolyte, pore size 6.5–8.5 Å) from Mirsid area (Salaj district, Romania) was a kind gift from Assoc. prof. M. Stanca from the Department of Chemical Technology, "Babes-Bolyai" University Cluj-Napoca, (Romania). The average granulation of the natural zeolite was 6.5 μm and its specific area was 2.25 m^2/cm^3. The synthetic zeolite, $Na_j[(AlO_2)_j(SiO_2)_{192-j}] \times z\ H_2O$; $z \sim 260$; $j = 77 \div 96$ (NaX type; pore size 4.3 Å; Si/Al ratio 1.5), was purchased from Bayer (Germany).

Hydrogen peroxide, $Na_2HPO_4 \cdot 2H_2O$ and $NaH_2PO_4 \cdot H_2O$ were purchased from Merck (Darmstadt, Germany). All other reagents were of analytical grade and used as received.

The supporting electrolyte was a 0.1 M phosphate buffer solution. The pH was adjusted in the interval 2–11 using appropriate H_3PO_4 or NaOH solution.

2.2. *Electrode preparation*

About 50 ml of a 0.01% (w/v) MG solution in water were shaken (3 days) with 50 mg of natural (NZ) or synthetic (SZ) zeolite. The modified zeolite was filtered, washed and dried. 25 mg of the modified zeolite were mixed with 25 mg graphite powder and 10 μl paraffin oil in order to obtain the modified carbon paste electrodes: MG-NZ-CPEs and MG-SZ-CPEs.

2.3. *Electrochemical measurements*

Electrochemical experiments were carried out using a typical three-electrode electrochemical cell. The modified carbon paste electrode was used as working electrode, a platinum ring as counter electrode and a saturated calomel electrode (SCE) or an Ag|AgCl/KCl_{sat} as reference electrode.

Cyclic voltammetry experiments were performed on a PC-controlled electrochemical analyzer (Autolab-PGSTAT 10, EcoChemie, Utrecht, The Netherlands). The charge amount (Q, F) involved in the redox response of the entrapped mediator for each modified electrode was evaluated from the integrated anodic or cathodic peak of the cyclic voltammograms recorded in the supporting electrolyte, at slow scan rate (10 mV s^{-1}), and corrected for the background current [21]. This parameter was used to compare the intensity and the stability of the electrochemical response of modified electrodes. The number of transferred electrons was assumed equal to 2 [11, 14, 15, 17].

Batch amperometric measurements at different H_2O_2 concentrations were carried out at an applied potential with 120 mV more negative than formal standard potential ($E^{0\prime}$) of the mediator, under magnetic stirring, using 0.1 M phosphate buffer solution (pH 7) as supporting electrolyte. The current–time data were collected using the above-mentioned electrochemical analyzer.

The experimental results are the average of at least three identically prepared electrodes, if not otherwise mentioned.

3. Results and discussion

3.1. *Electrochemical behavior of zeolite modified carbon paste electrodes*

As it can be observed from Figure 1, only NZ-CPEs exhibit some electrochemical activity. The peak pair observed at NZ-CPEs in contact with the supporting electrolyte ($E^{0\prime}$ = 210 mV *vs.* SCE) was attributed to Fe ions, supposed to be in the natural zeolite. In order to

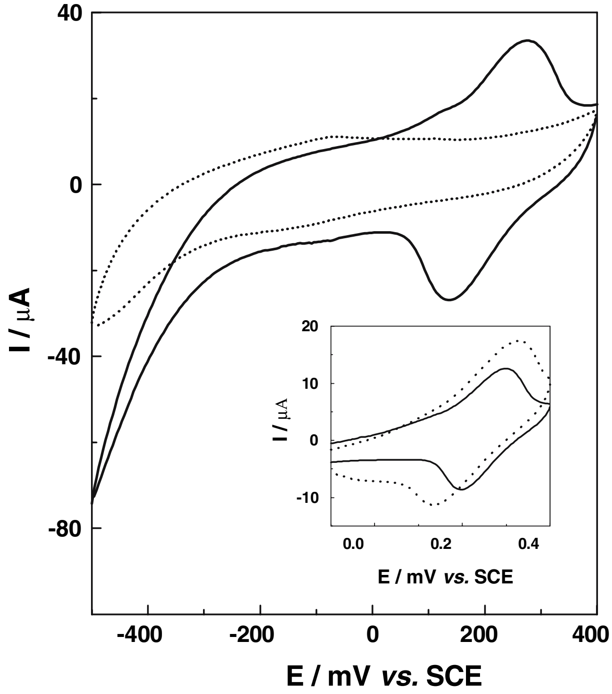


Fig. 1. Cyclic voltammograms for NZ-CPEs (—) and SZ-CPEs (····) recorded in supporting electrolyte; effect of $FeCl_3$ addition (····) on the voltammetric response of NZ-CPEs (inset). Experimental conditions: starting potential, −500 mV *vs.* SCE; potential scan rate, 50 mV s^{-1} and 10 mV s^{-1} (inset); supporting electrolyte, 0.1 M phosphate buffer, pH 3.0.

confirm this supposition, the NZ-CPEs were tested in the same supporting electrolyte, containing 10^{-2} M $FeCl_3$. The increase of peak current observed in the presence of $FeCl_3$ (inset) confirmed that these peaks belong to Fe^{2+}/Fe^{3+} couple existing inside the natural zeolite. Additionally, this hypothesis was proved by the presence of Fe peak in the EDS spectrum (Princeton Gamma Tech. energy dispersive X-ray analyzer coupled with a scanning electronic microscope) (results not shown).

The immobilized MG exhibits a peak pair for both investigated ZMEs (Figure 2). The electrochemical parameters, corresponding to the voltammetric response attributed to the following reaction [11, 14, 15, 17]:

$$MGH \leftrightarrow MG^{+} + 2e^{-} + H^{+} \quad (1)$$

are presented in Table 1.

A supplementary peak pair (formal standard potential, $E^{0\prime} = -230$ mV *vs.* Ag|AgCl/KCl_{sat}) appears only on the voltammograms recorded at MG-SZ-CPEs (Figure 2). This behavior was attributed to the presence of methylene blue as impurity in the MG. This explanation was first suggested by Kulys et al. [10], taking into account the $E^{0\prime}$ value for dissolved methylene blue (−245 mV *vs.* SCE, pH 8). The absence of this peak pair in the case of MG-NZ-CPEs should be due to the lower amount of entrapped MG, in comparison with SZ (see Table 1 for *Q* measured for the peak pair placed at −14 mV *vs.* Ag|AgCl/KCl_{sat}), probably as a consequence of its higher granulation (see TEM micrographs from Figure 3) and its larger pores size. It is noteworthy to mention that the difference between the *Q* values, estimated for MG in the case of MG-SZ-CPEs and of MG-NZ-CPEs, was obtained in the same experimental conditions (the mediator concentration in the modifying solution and the amount of zeolite). This indicates a stronger adsorption of MG onto the synthetic zeolite.

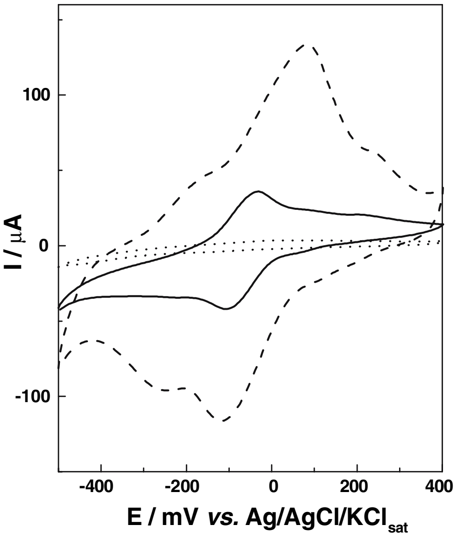


Fig. 2. Cyclic voltammograms for NZ-CPEs (····), MG-NZ-CPEs (—) and MG-SZ-CPEs (—). Experimental conditions: starting potential, −500 mV *vs.* Ag|AgCl/KCl_{sat}; potential scan rate, 10 mV s^{-1}; supporting electrolyte, 0.1 M phosphate buffer, pH 7.0.

Table 1. Electrochemical parameters of the voltammetric response for MG-zeolite-modified CPEs

Electrode	$E^{0\prime}$ (mV *vs.* Ag|AgCl/KCl_{sat})	ΔE_{peak} (mV)	I_{pa}/I_{pc}	Q (10^9 F)
MG-NZ-CPEs	−67	66	1.4	7.1
MG-SZ-CPEs	−230[a]	86	0.5	2.8
	−14	256	0.9	28

Experimental conditions: as in Figure 2.
[a]Attributed to the presence of methylene blue impurity.

The values of ΔE_{peak} and $|I_{pa}/I_{pc}|$ ratio (Table 1) for the MG peak pair, placed in the optimal potential domain for H_2O_2 amperometric detection [19], point to the existence of a quasi-reversible behavior for both MG-NZ-CPEs and MG-SZ-CPEs. However, the peaks split for both electrodes are much larger than that reported for MG adsorbed on graphite (ca. 20 mV) [11], indicating a diffusional behavior of the entrapped mediator. At the same time, the electrochemical parameters summarized in Table 1 suggest a slower electron transfer rate in the case of MG adsorbed on zeolites and incorporated into carbon paste, or the existence of uncompensated ohmic drop due to the higher electric resistance of the zeolite modified CPEs.

A positive shift of the $E^{0\prime}$ values for MG adsorbed on both zeolites was observed (Table 1) as compared with the $E^{0\prime}$ values reported for dissolved MG (−110 mV *vs.* SCE, at pH 8.02) [10]. This effect should be due to the interactions between the entrapped MG and the negatively charged zeolitic matrix.

According to reaction (1) the $E^{0\prime}$ value of MG should be pH dependent. This behavior was observed in the case of MG-NZ-CPEs. For these electrodes, the slope of regression line corresponding to the $E^{0\prime}$ *vs.* pH dependence (pH 5–9) was 0.021 V/ΔpH, indicating a $2e^{-}/1H^{+}$ transfer involved in the redox process. This result is in agreement with that reported for MG adsorbed on graphite (pH 6.5–11) [11] and montmorillonite (pH 5.4–9) [15].

Surprisingly, for MG-SZ-CPEs, in the pH range from 3 to 10, the $E^{0\prime}$ value does not change significantly with the pH (Figure 4). This result is similar to those obtained for (i) MG [17] and other redox mediators [22, 23] adsorbed on zirconium phosphate, for NADH electrocatalytic oxidation and (ii) methylene blue immobilized on a mordenite type zeolite for ascorbic acid mediated electrooxidation [9]. As suggested [9], the mediator entrapment into the channels of zeolite in a confined position, where the acidity of the environment surrounding the dye does not change with the solution pH, could be a reasonable cause for the independence of $E^{0\prime}$ towards pH variation. The other explanation, formulated in the case of zirconium phosphate adsorbent, based on the protonation/deprotonation equilibrium of the redox mediator [24], seems to be not relevant in the case of the zeolite-modified CPEs.

Cyclic voltammetric measurements were performed in a range of potential scan rate from 0.01 to 1.6 V s^{-1}, for both electrodes in contact with phosphate buffer

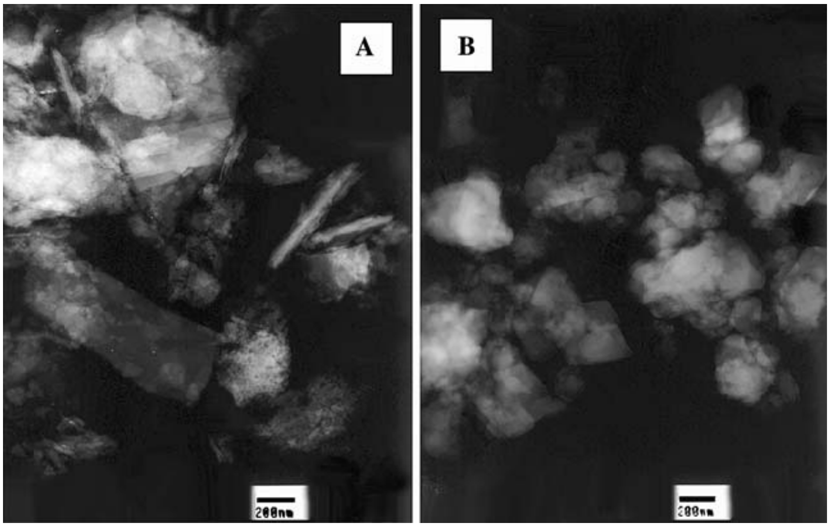


Fig. 3. TEM micrographs of NZ (A) and SZ (B).

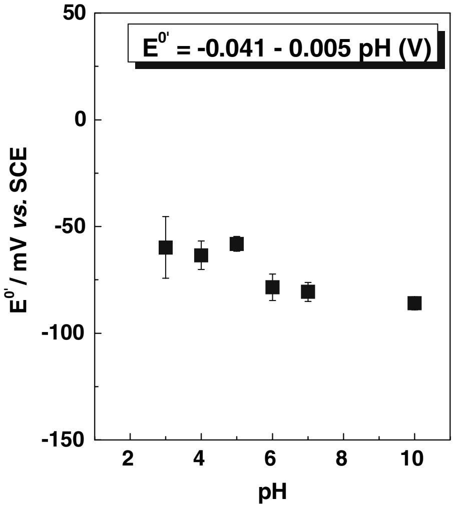


Fig. 4. Variation of $E^{0\prime}$ with pH for MG-SZ-CPEs. Experimental conditions: starting potential, −500 mV *vs.* Ag|AgCl/KCl$_{sat}$; potential scan rate, 10 mV s^{-1}; supporting electrolyte, 0.1 M phosphate buffer.

Table 2. Parameters of the log–log linear regression corresponding to the peak current dependence on the potential scan rate for MG-NZ-CPEs (0.01–0.8 V s^{-1}) and for MG-SZ-CPEs (0.01–3.2 V s^{-1})

Electrode	Slope		R/no. of exp. points	
	Oxidation	Reduction	Reduction	Oxidation
MG-NZ-CPEs	0.39 ± 0.01	0.48 ± 0.01	0.9978/10	0.9965/10
MG-SZ-CPEs	0.40 ± 0.01	0.51 ± 0.01	0.9973/15	0.9915/15

Experimental conditions: as in Figure 2.

solutions of different pHs (5–9). A linear dependence of the anodic and cathodic peak current (I_p) on $v^{1/2}$ (v is the potential scan rate) was observed (Table 2), suggesting that the desorbed electroactive species can diffuse freely to the surface of carbon grains during the redox process [25]. However, it is important to mention that the redox dye is not effectively removed from the zeolite [9].

From the variation of peak potentials with potential scan rate (Figure 5), using the treatment proposed by Laviron [20], the heterogeneous electron transfer rate constant (k_s, s^{-1}) was estimated for MG-NZ-CPEs and MG-SZ-CPEs, at different pH values (Table 3). As can be observed, the k_s values for MG-NZ-CPEs are higher than for MG-SZ-CPEs, reflecting once more a lower interaction between MG and NZ than between MG and SZ. On the other hand, the k_s values, as well as the transfer coefficient (α), slightly decrease with increase in supporting electrolyte pH. In comparison with other k_s values published for modified electrodes based on phenothiazine derivatives mediators [22, 23, 26] the values reported here are of the same order of magnitude.

The stability of modified electrodes was tested under potentiodynamic conditions, by continuous cycling of the electrode potential (100 cycles), in the potential range corresponding to the MG redox activity (± 120 mV around its standard formal potential), at pH 7. For both modified electrodes, a slight progressive decrease of the charge amount (Q) involved in the redox response was observed, while the shape of the recorded voltammograms remained practically invariant (results not shown). The Q *vs.* t linear dependence indicates that the decrease of the electrode voltammetric response obeys pseudo-zero-order kinetics [27]. This behavior reflects that all active centers existing on the electrode surface are saturated with mediator molecules, due to the presence of a large amount of MG entrapped in the zeolite matrix, which ensures the continuous supply of the perielectrodic space with MG molecules. The rate constants of the electrodes deactivation process (k_{deact}) were estimated as the slope of Q *vs.* t plots (Table 4). As expected, the electrodes deactivation is mainly controlled by the oxidation step. It is noteworthy that MG-SZ-CPEs present a better electrochemical stability than MG-NZ-CPEs. This corroborates the statements

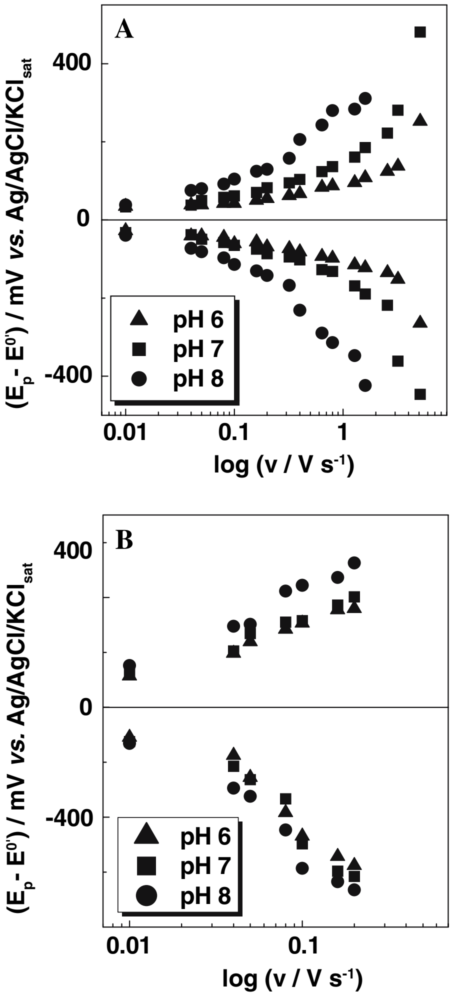


Fig. 5. Experimental dependence of $(E_p–E^{o'})$ on the logarithm of the scan rate for MG-NZ-CPEs (A) and MG-SZ-CPEs (B). Experimental conditions: starting potential, −500 mV *vs.* Ag|AgCl/KCl$_{sat}$; supporting electrolyte, 0.1 M phosphate buffer.

Table 3. Kinetic parameters for the heterogeneous electron transfer at MG-Z-modified CPEs

Electrode	pH	k_s (s^{-1})	α	R/no. of exp. points	
				Oxidation	Reduction
MG-NZ-CPEs	5	4.5	0.83	0.9919/6	0.9991/6
	7	4.5	0.51	0.9915/5	0.9930/5
	9	3.9	0.40	0.9891/4	0.9829/4
MG-SZ-CPEs	5	0.58	0.34	0.9774/6	0.9887/6
	7	0.31	0.21	0.9800/6	0.9784/6
	8	0.28	0.29	0.9751/6	0.9759/6

Experimental conditions: as in Figure 5.

formulated above concerning the electrochemical behavior of MG ($E^{0\prime}$- pH dependence and electron transfer kinetics) when adsorbed on NZ and SZ and the structural data of the two zeolites. On the other hand, the small values of deactivation rate constants estimated for both modified electrodes prove their relative good electrochemical stability in the potential window recommended for H_2O_2 detection.

Table 4. Deactivation parameters corresponding to MG-zeolite-modified CPEs

Electrode	k_{deact} (10^{10} F s^{-1})		R/no. of exp. points	
	Oxidation	Reduction	Oxidation	Reduction
MG-NZ-CPEs	6.8	2.6	0.9970/3	0.9811/4
MG-SZ-CPEs	0.25	0.18	0.9900/5	0.9948/3

Experimental conditions: potential scan rate, 10 mV s¯1; supporting electrolyte, 0.1 M phosphate buffer (pH 7).

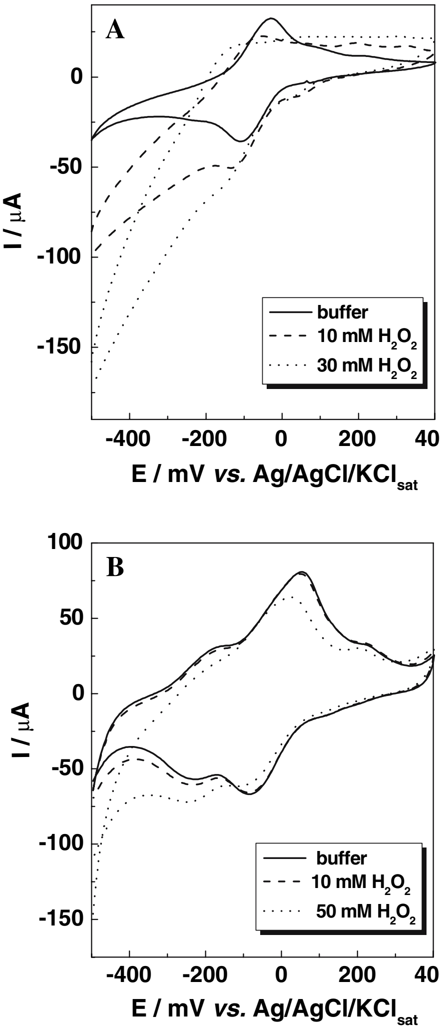


Fig. 6. Cyclic voltammograms recorded at MG-NZ-CPEs (A) and MG-SZ-CPEs (B) in the absence and in the presence of H_2O_2 (non dearated solution). Experimental conditions: as in Figure 2.

3.2. *Electrocatalytic reduction of H_2O_2*

Based on the favorable electrochemical behavior of MG-NZ-CPEs and MG-SZ-CPEs ($E^{0\prime}$ close to 0 V *vs.* Ag|AgCl/KCl$_{sat}$), the electrocatalytic activity of the two modified electrodes towards H_2O_2 reduction was investigated using cyclic voltammetry. As can be seen from the cyclic voltammograms recorded at MG-modified zeolite-CPEs in the absence and in the presence of different concentrations of H_2O_2 (Figure 6), the best electrocatalytic activity was observed in the case of MG-NZ-CPEs. Consequently, only MG-NZ-CPEs were selected for all further experiments.

This higher electrocatalytic activity is due to the presence of MG and not to the iron content in NZ. This statement is based on the difference between the peak potential corresponding to the Fe^{3+} reduction ($E_{p,c}$ = 150 mV *vs.* SCE; Figure 1) and that corresponding to H_2O_2 electrocatalytic reduction ($E_{p,c}$ = −110 mV *vs.* Ag|AgCl/KCl_{sat}; Figure 6A).

In comparison with the H_2O_2 reduction on zeolite-modified CPEs without MG (results not shown), a positive shift of the H_2O_2 reduction potential of about 120 mV *vs.* Ag|AgCl/KCl_{sat} was observed for MG-NZ-CPEs. The electrocatalytic efficiency ($I_{catalytic}/I_0$) of MG-NZ-CPEs, estimated from CV measurements performed in the presence of 10 mM H_2O_2, was equal to 1.7 for MG-NZ-CPEs (at –124 mV *vs.* Ag|AgCl/KCl_{sat}).

Batch amperometric measurements at constant applied potential (−180 mV *vs.* Ag|AgCl/KCl_{sat}) proved that MG-NZ-CPEs work well as H_2O_2 amperometric sensors (Figure 7). A typical example of stable and fast amperometric response to successive injections of 1 mM H_2O_2 is presented in Figure 7A.

By analogy with an enzymatic reaction, the amperometric calibration data (Figure 7B) were fitted using the Michaelis–Menten equation, and the following kinetic parameters were found: K_M = 18 mM and I_{max} = 60 μA. At the same time, the analytical parameters were estimated as follows: the sensitivity (calculated as I_{max}/K_M ratio) ~ 3.35 mA M^{-1}; the linear range, from 1.5 μM to 1 mM; the detection limit of 0.5 mM (for a signal to noise ratio of 3); the response time, ~20 s.

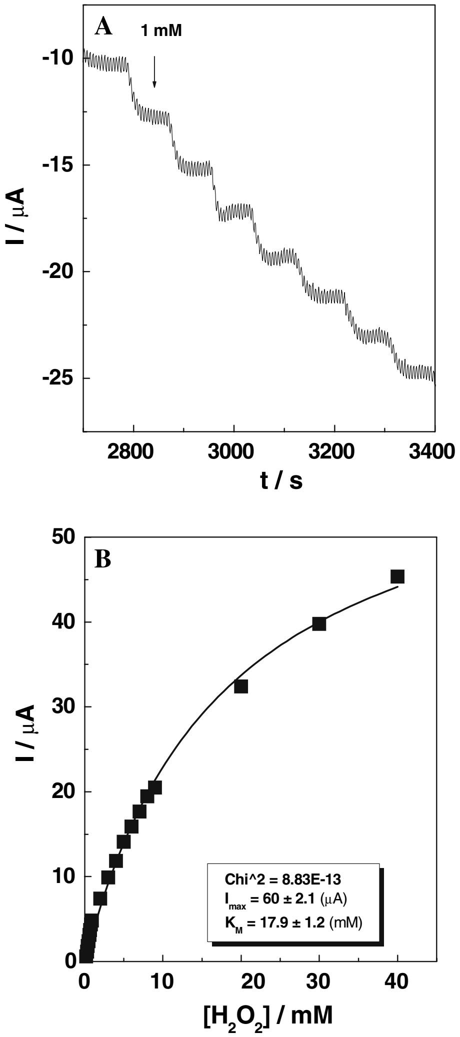


Fig. 7. Amperometric response to successive increments of 1 mM H_2O_2 (A) and the calibration curve for H_2O_2 (B) at MG-NZ-CPEs. Experimental conditions: applied potential, −180 mV *vs.* Ag|AgCl/KCl_{sat}; supporting electrolyte, 0.1 M phosphate buffer, (pH 7.0), non dearated solution; magnetic stirring.

4. Conclusions

This work represents, to our best knowledge, the first comparative electrochemical study focused on the influence of zeolite structure on the redox response of adsorbed MG entrapped in a carbon paste matrix. The pH dependence on the formal standard potential, the magnitude of the electron transfer rate constants, the electrode response decay and the electrocatalytic efficiency served as terms of comparison. It was concluded that in order to obtain efficient MG-modified carbon paste electrodes for H_2O_2 amperometric detection, the best choice between the two investigated zeolites was the natural one.

The NZ is characterized by the highest pore and grain size, suggesting that beside its role to increase the hydrophilicity of the carbon paste matrix [2], the zeolite acts as a simple mediator reservoir. The MG molecules are retained within the NZ matrix by electrostatic interactions with the zeolite cage. At the NZ modified electrode/electrolyte interface, the charges are transferred mainly *via* an extrazeolitic mechanism, involving two steps [2]: (i) an ion exchange process between the immobilized positively charged MG species and the supporting electrolyte cations; (ii) an electron transfer process occurring between the free MG species and the graphite grains from the carbon paste. In the case of SZ-modified electrodes, the slower rate of the charge transfer process across the modified electrode interface (see the k_s values in Table 3) should be correlated with the particular structural characteristics of SZ (porosity, grain size etc.), and suggests a charge transfer mechanism, partially based on a surface-mediated electron transfer [2].

Acknowledgements

The authors thank Assoc. prof. Maria Stanca (Department of Chemical Engineering and Chemical Technology, “Babes-Bolyai” University Cluj-Napoca, Romania) for provision and characterization of the natural zeolite. They are also grateful to Dr. Georges Maurin (Université Pierre et Marie Curie, Laboratoire Interfaces et Systèmes Electrochimiques, Paris, France) for EDS spectra and TEM micrographs. Financial support from CNCSIS (Grant A 39/349-2006), Romanian Academy (GAR 44-2006) and CEEX (ET 50-2006) is gratefully acknowledged.

References

1. D. Rolison, *Chem. Rev.* **90** (1990) 867.
2. A. Walcarius, *Anal. Chim. Acta* **384** (1999) 1.
3. D.R. Rolison, R.J. Nowak, T.A. Welsh and C.G. Murray, *Talanta* **38** (1991) 27.
4. J. Lipkowski and P. Ross, ‚The Electrochemistry of Novel Materials' (VCH Publishers Inc., NY, 1994), pp. 339–380.
5. A. Walcarius, *Electroanalysis* **8** (1996) 971.
6. B. Liu, F. Yan, J. Kong and J. Deng, *Anal. Chim. Acta* **386** (1999) 31.
7. B. Liu, Z. Liu, D. Chen, J. Kong and J. Deng, *Fresenius J. Anal. Chem.* **367** (2000) 539.
8. S. Serban and N.E. Murr, *Biosens. Bioelectron.* **20** (2004) 161.
9. M. Arvand, S. Sohrabnezhad, M.F. Mousavi, M. Shamsipur and M.A. Zanjanchi, *Anal. Chim. Acta.* **491** (2003) 193.
10. J. Kulys, G. Gleixner, W. Schuhmann and H.-L. Schmidt, *Electroanalysis* **5** (1993) 201.
11. Q. Chi and S. Dong, *Anal. Chim. Acta* **285** (1994) 125.
12. Q.-J. Chi and S.-J. Dong, *J. Mol. Catal. A: Chem.* **105** (1996) 193.
13. B. Wang and S. Dong, *Talanta* **51** (2000) 565.
14. H. Liu, Y. Liu, J. Qian, T. Yu and J. Deng, *Talanta* **43** (1996) 111.
15. C. Lei and J. Deng, *Anal. Chem.* **68** (1996) 3344.
16. A.R. Lucca, A.S. Santos, A.C. Pereira and L.T. Kubota, *J. Colloid Interface Sci.* **254** (2002) 113.
17. F.D. Munteanu, L.T. Kubota and L. Gorton, *J. Electroanal. Chem.* **509** (2001) 2.
18. D.-M. Zhou, H.-Q. Fang, H.-Y. Chen, H.-X. Ju and Y. Wang, *Anal. Chim. Acta* **329** (1996) 41.
19. L. Gorton, *Electroanalysis* **7** (1995) 23.
20. E. Laviron, *J. Electroanal. Chem.* **101** (1979) 19.
21. R.W. Murray, *In* Bard A.J. (ed.), ‚Electroanalytical Chemistry' (Marcel Dekker, New York, 1984), pp. 191.
22. F.D. Munteanu, D. Dicu, I.C. Popescu and L. Gorton, *Electroanalysis* **15** (2003) 383.
23. D. Dicu, F.D. Munteanu, I.C. Popescu and L. Gorton, *Anal. Lett.* **36** (2003) 1755.
24. A. Clearfield, *Chem. Rev.* **88** (1988) 125.
25. A.J. Bard and L.R. Faulkner, ‚Electrochemical Methods. Fundamentals and Applications' (J. Wiley, New York, 1980), pp. 218.
26. D. Gligor, L. Muresan, I.C. Popescu and I.A. Silberg, *Rev. Roum. Chim.* **47** (2002) 953.
27. A. Ciszewski and G. Milczarek, *Anal. Chem.* **72** (2000) 3203.