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Zeolite-modified solid carbon paste electrodes

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Abstract New zeolite-modified carbon-based electrodes are described. They are based either on the physical anchoring of zeolite particles on the surface of solid carbon paste (the viscosity of which can be tuned by temperature change or controlled dissolution by an organic solvent), or on the dispersion of zeolite particles in the bulk of a carbon paste matrix containing solid paraffin as a binder. Both these systems display superior electrochemical performance in comparison to corresponding “classical” zeolite-modified carbon paste electrodes using mineral oil as binder. These well-described composites usually suffer from poor mechanical stability in stirred media as well as memory effects due to significant ingress of the external solution into the bulk electrode. Advantages of the zeolite-modified solid carbon paste electrodes are reported mostly on the basis of two electroanalytical applications: the voltammetric detection of Cu^{2+} ions after accumulation by ion exchange at open circuit, and the indirect amperometric detection of non-electroactive species (i.e. Na^+) in flow injection analysis.

Keywords Flow injection analysis · Modified electrodes · Preconcentration · Solid carbon paste electrodes · Zeolites

Introduction

Zeolite-modified electrodes (ZMEs) have attracted considerable attention during the past 15 years because they combine in a single device the specificity of charge transfer reactions with the intrinsic properties of the aluminosilicates, such as molecular sieving and ion exchange [1, 2, 3, 4, 5, 6, 7]. This unique feature of ZMEs has led to various advanced applications, including preconcentration and molecular recognition or discrimination, electrocatalysis, dispersion electrolysis, indirect amperometric detection, biosensors, potentiometry, energy storage, and photoelectrochemistry [8]. Among them, electroanalysis holds a prominent place, and most works in this field have been performed using zeolite-modified carbon paste electrodes [9, 10].

A critical point in applying ZMEs in electrochemical science is their preparation. Zeolites are insulating materials so that their implication in electrochemistry requires close contact to an electronically conducting substrate. On the other hand, zeolites do exist most often as fine powders made of individual crystals of micrometric size, and their molding into well-shaped homogeneous three-dimensional arrangements (e.g. at electrode surfaces) is therefore not easy. Three major approaches are often reported: (1) zeolite-polymer films coated on solid electrode surfaces, where the polymer acts as a binder to stick together the zeolite particles (e.g. [11, 12, 13]) (an alternative is the dense zeolite monograin layer covered by a thin polystyrene film [14]); (2) binder-free ZMEs based on dry graphite-zeolite mixtures pressed on a stainless steel grid [15, 16]; and (3) zeolite-modified carbon paste electrodes, where zeolite particles are dispersed within a mixture of graphite powder and mineral oil binder (ZMCPEs) [17, 18, 19].

Even if successful applications in electroanalysis are achieved with ZMCPEs (e.g. voltammetric analysis after preconcentration [20, 21, 22], indirect amperometric detection in flowing streams [23, 24], biosensors [25, 26],

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electrocatalysis [27]), some problems may arise in the case of prolonged use. Indeed, if such an electrode is soaked in an aqueous solution for a long time, significant impregnation in the bulk paste occurs owing to the hydrophilic character of the zeolite particles [18, 25], which may induce undesirable memory effects when performing successive experiments with the same electrode surface. The wetted section of ZMCPEs was found to increase with the immersion time in solution [18], especially with hydrophilic zeolites [26]. Making the zeolite more hydrophobic (i.e. by dealumination [26]) is a possible way to circumvent the impregnation, but this leads to solids with restricted (or even without) ion exchange properties and, therefore, less interesting for use as electrode modifiers. Another strategy is to scale down the thickness of the zeolite-containing composite electrode, which can be achieved via the production of disposable electrodes by screen printing a zeolite-based carbon ink onto a ceramic substrate [28]. The resulting screen-printed zeolite-carbon strips are composite films characterized by a typical thickness of 200 μm and containing zeolite particles embedded in a carbon-polymer matrix. They usually give better performance than the corresponding ZMCPEs (faster preconcentration and better regeneration [28]), but they are not totally free of memory effects when applied to successive voltammetric analyses after preconcentration.

In the goal to improve further the behavior of carbon-based zeolite-modified electrodes, we have evaluated here the advantage of using solid paraffin instead of mineral oil to prepare ZMCPEs. Chemically modified solid carbon paste electrodes, which were introduced by the Kauffmann group [29], have been already described for electroanalytical purposes (e.g. chemical sensors [30, 31, 32, 33, 34, 35], electrocatalysis [36], biosensors [37, 38, 39, 40]); they usually display longer operational stability, higher robustness, and better electrochemical performance than those prepared using a liquid binder [29, 37, 38]. In the field of ZMEs, this solid matrix appears attractive for two reasons: the possibility to tune the viscosity of the paste by monitoring the temperature, and the higher lipophilicity of the electrode material made of a solid paraffin instead of mineral oil. The former would lead to durable immobilization of zeolite particles at the electrode surface, while the latter would prevent impregnation from the solution in the bulk electrode.

We assess in this work the benefit of the incorporation of highly hydrophilic zeolite particles at the surface of or within solid carbon paste electrodes for improving the performance of ZMCPEs in electroanalysis, via two target applications: the accumulation of copper(II) (used here as a model analyte) prior to its voltammetric detection, and the indirect amperometric detection of non-electroactive species in flow injection analysis. Advantages of zeolite-modified solid carbon paste electrodes over those based on the "conventional" carbon paste matrix will be discussed.

Experimental

A model 263 potentiostat (EG&G, Princeton Applied Research) was used to perform the voltammetry experiments. It was equipped with a three-electrode system mounted on a 50-mL cell. The counter electrode was a platinum wire and a calomel electrode (Radiometer, XR 110) served as reference. Working electrodes were homemade zeolite-modified solid carbon paste electrodes (solid ZMCPEs). Zeolite Y was the Linde molecular sieve cat. base L-Y54 powder (sodium form; average particle size 0.5–2 μm ; chemical composition $\text{Na}_{56}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}\cdot 250\text{H}_2\text{O}$) obtained from UOP, Molecular Sieve Division. All solutions were prepared with high-purity water (resistivity 18 $\text{M}\Omega\text{ cm}$) obtained from a Millipore Milli-Q water purification system. All chemicals were analytical grade.

Several kinds of solid ZMCPE were prepared. Film-based electrodes were produced by dropping typically 20 μL of a zeolite suspension (350 mg L^{-1} in ethanol) onto the surface of solid carbon paste electrodes, and allowing the solvent to evaporate slowly at room temperature. Two kinds of solid carbon pastes were used for this purpose: one made of a 10:90 mass ratio of ketjenblack (EC-600, Akzo Chemie, Belgium) and solid paraffin wax (m.p. 58–60 $^{\circ}\text{C}$, Fluka), and the other made of 40% solid paraffin and 60% high-purity graphite (Ultra F, < 325 mesh, Alfa). Heating the electrode surface, by placing a hot ceramic plate above it at approximately 1 cm, was also performed to consolidate the anchorage of zeolite particles (swallowing in the viscous medium during heating, and physical immobilization in the solid matrix upon cooling). Bulk solid ZMCPEs were prepared by adding 0.4 g of solid paraffin to 0.6 g of a homogeneous mixture of zeolite and graphite particles (1:5 ratio). This three-component mixture was heated above 60 $^{\circ}\text{C}$ to make it viscous and enable appropriate homogenization. The "hot" paste was packed into the end of an Altuglas cylindrical tube including electrical contact. Upon cooling to room temperature, the electrode surface was polished on a paper. "Conventional" zeolite-modified carbon paste electrodes were also used for comparison purposes. They were prepared as previously described [18] by mixing 10% zeolite, 60% high-purity graphite, and 30% mineral oil (Aldrich) thoroughly until a uniformly wetted paste was obtained. Portions of them were then packed into the end of a homemade PTFE cylindrical tube equipped with a screwing stainless steel piston. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing it on a piece of weighing paper. Surface hydrophobicity was evaluated by dropping 1 μL of water on the electrode and measuring the contact angle using a Goniometer (model VCA 2500 XE).

The general procedure for preconcentration analysis of copper(II) includes an accumulation step achieved by immersing the electrode in stirred solutions containing the target analyte at a given concentration, followed by medium exchange into a separate voltammetric cell containing the supporting electrolyte (0.1 M NaNO_3) where a potential of -0.5 V was held during 60 s under quiescent conditions prior to recording the anodic stripping voltammograms in the linear scan mode (rate 20 mV s^{-1}). No regeneration of the electrode surface was performed after each detection step in order to evaluate the reproducibility in successive experiments at a single electrode. The "memory" effect was characterized by recording one (or several) detection signals in addition to the first one, in the same experimental conditions, but omitting the preconcentration step.

For the indirect amperometry experiments performed in flow injection configuration, the solid ZMCPE was mounted on a homemade flow-through electrochemical detector, as was previously described for conventional carbon paste [24]. In this case, however, a solid ZMCPE was used, containing zeolite particles ion exchanged with electroactive copper(II) species. The carrier flow (pure water) was laid on the electrode surface by a model 420 HPLC pump connected with a model 460 HPLC Autosampler (Kontron). Injections were made using a 25- μL sample loop. Flow injection amperograms were plotted using a x - y - t recorder (Philips

PM8271). The copper form of zeolite NaY was prepared by suspending 2 g of the solid in a 250 mL solution containing 0.1 M $\text{Cu}(\text{NO}_3)_2$ and allowing the suspension to react under constant stirring for 48 h. The solid particles were then filtered, copiously washed with pure water, and allowed to dry in air at room temperature before incorporation in the carbon paste. Their Cu^{2+} content was 1.4 mmol g^{-1} .

Results and discussion

Basic characterization

The basic idea of this work is to obtain a zeolite-modified carbon paste electrode for which the electrochemical response is due solely to the zeolite particles located at the electrode surface; bulk located particles should ideally not be involved (as they are with conventional ZMCPEs) [18, 25]. A straightforward way is to deposit a zeolite layer on the carbon paste surface while ensuring their physical attachment to avoid leaching into the surrounding solution. This might be achieved by depositing zeolite particles onto the surface of a solid carbon paste electrode and heating this surface to lime the solid particles in the composite matrix due to the higher viscosity, leading to their physical anchoring.

A first attempt was made by dropping an aliquot of zeolite suspended in water, but the hydrophobic character of the carbon paste prevented the homogeneous deposition (zeolite particles gathered in the center of the electrode surface as a result of the slow evaporation of the water drop). Moreover, the zeolite particles did not "stick" to the electrode surface, in agreement with the necessity to use a polymer overcoating when attempting to form a zeolite layer on the surface of a solid electrode [14]. Even after thermal treatment the solid particles were easily removed from the electrode in stirred solution. Better results were obtained when forming the zeolite layer by using particles suspended in ethanol because of better wettability. Such deposition was performed on both graphite-based and ketjenblack-containing carbon paste electrodes. Zeolite particles loaded either with Ag^+ or Cu^{2+} species were used in order to evaluate their relative performance by cyclic voltammetry. Better reproducibility was obtained with graphite-based electrodes (based on the current intensity of the anodic stripping peak): 20% standard deviation from one graphite-based electrode to another ($n=5$), and 45% for the zeolite films coated on ketjenblack-based electrodes ($n=5$). This result can be partly explained by the poor adhesion of the ketjenblack-based paste to the electrode body, leading to undesired percolation effects. On the other hand, a better signal-to-noise ratio was obtained with zeolite films on ketjenblack-containing electrodes, displaying well-shaped signals and lower capacitive currents (Fig. 1, comparison of curves a and b). Contrary to what was observed with conventional ZMCPEs [18, 19], successive multisweep cyclic voltammetry applied to both films resulted in a fast decrease in peak current, which is indicative of the absence of

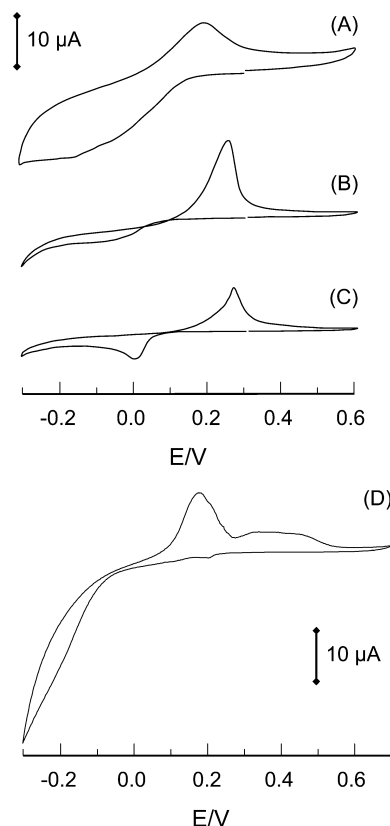


Fig. 1A–C Cyclic voltammograms recorded at various silver-exchanged ZMCPEs in 0.1 M KNO_3 (electrode diameter 3 mm; scan rate 10 mV s^{-1}): **A** zeolite film on graphite-based solid CPE; **B** zeolite film on ketjenblack-based solid CPE; **C** bulk zeolite-modified solid carbon paste electrode. **D** Cyclic voltammogram recorded at copper-exchanged bulk ZMCPEs at 50 mV s^{-1}

significant dissolution of the bulk paste by the external solution.

In a second step, graphite-based solid carbon paste electrodes containing zeolite particles dispersed in the bulk composite were prepared and tested by similar cyclic voltammetry experiments. The corresponding systems based on ketjenblack instead of graphite did not give satisfactory results because of the difficulty to mix homogeneously two kinds of solids displaying so different densities (0.1 for ketjenblack and 1.9 for zeolite). Solid ZMCPEs loaded with, for instance, Ag^+ species gave rise to well-defined signals (Fig. 1, curve c) and a better signal-to-noise ratio than the films. Reproducibility of their preparation was also better than that for zeolite film electrodes (8% standard deviation for $n=5$). Surprisingly, and interestingly, multisweep cyclic voltammetry also gave rise to a fast decrease in peak currents, indicating that no significant impregnation of the bulk paste had occurred, contrary to ZMCPEs based on mineral oil [18, 19]. This improvement is attributed to the solid paraffin which prevents the solution reaching zeolite particles located deeper in the composite matrix. In this case, only the zeolite particles located on the electrode surface, i.e. at the electrode/solution interface, are liable to be wetted by the surrounding solution.

Contact-angle measurements at a water drop deposited on the surface of bare and zeolite-modified solid carbon paste electrodes gave very close values: 112° in the absence of zeolite and 108° for the ZMCPE. This indicates that the hydrophilic character of zeolite particles does not induce a dramatic decrease in the carbon paste hydrophobicity. The solid ZMCPE-containing zeolite particles in the bulk therefore also appear suitable, as film-based electrodes, to overcome the impregnation effects usually observed at conventional ZMCPEs. Similar trends were observed using copper(II) as the electroactive probe, except that an additional stripping signal occurs after the main one, as illustrated by curve d in Fig. 1. This behavior is well known when large metallic copper deposits are formed at the surface of carbon paste electrodes [41], but the additional signal disappears in less concentrated conditions, as shown hereafter (Fig. 2).

Batch preconcentration analysis: the case of copper(II)

Relative sensitivity and memory effects

Figure 2 compares the sensitivity of film-based and bulk ZMCPEs with respect to the detection of Cu^{2+} species by anodic stripping voltammetry after accumulation by ion exchange at open circuit. A potential scan rate of 20 mV s^{-1} was selected as a good compromise between a rather high sensitivity and a half-peak width not too large (significant peak enlargement was observed at higher scan rates). The peak intensity is related to both the ability of the composite electrode to preconcentrate the analyte within the zeolite particles located at the electrode surface, and the efficiency of the electrochemical detection step. As shown, the zeolite layer coated on the ketjenblack-based electrode gave rise to rather a low current response, in the form of a wide stripping peak (Fig. 2, curve B). Similar zeolite coatings on graphite-based solid paste displayed narrower signals with higher intensity (Fig. 2, curve A₁), which was however found to decrease dramatically upon heating the electrode surface to obtain durable anchoring

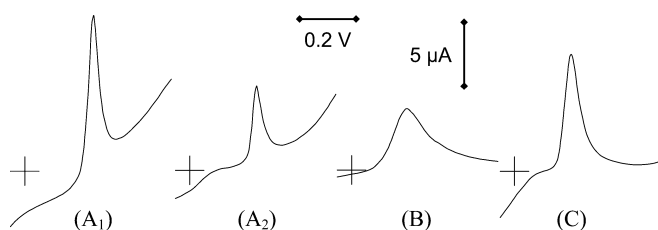


Fig. 2 Anodic stripping voltammograms recorded at various ZMCPEs in 0.1 M KNO_3 after 2-min accumulation at open circuit from a $1 \times 10^{-4} \text{ M}$ copper(II) solution, 60 s electrolysis at -0.5 V , and scanning potentials at a 20 mV s^{-1} rate up to $+0.5 \text{ V}$. A₁ Zeolite film on graphite-based solid CPE; A₂ same as A₁ after thermal treatment of the electrode surface; B zeolite film on ketjenblack-based solid CPE; C bulk zeolite-modified solid carbon paste electrode. The cross indicates the origin 0.00 V , zero current

of zeolite particles in the solid composite (Fig. 2, curve A₂). This decrease is explained by larger amounts of hydrophobic paraffin surrounding the zeolite particles (due to absorption when melting the solid binder) that hinder somewhat the wettability of the electrode surface in aqueous media. Note that the thermal treatment was not absolutely necessary to immobilize zeolites at the electrode surface as their deposition from an ethanol suspension is accompanied by some dissolution of the paraffin, which is amenable to coprecipitation with zeolite particles during solvent evaporation. Anyway, it was found that this treatment is required in fact to maintain the electrode activity over prolonged periods of time, whereas untreated zeolite films underwent a significant decrease in sensitivity upon successive measurements (i.e. 70–80% loss after 15 “preconcentration-detection” sequences). Solid ZMCPE-containing zeolite particles dispersed in the bulk of the paste did not suffer from this drawback because their preparation involves intimate contact between all the components of the composite electrode. This electrode was characterized by nearly the same sensitivity (Fig. 2, curve C) as that of the best zeolite film. Because of this comparable performance, its better reproducibility, and ease of preparation, this bulk ZMCPE prepared from solid paraffin (solid ZMCPE) was used throughout and compared to the corresponding “classical” or “conventional” ZMCPE based on mineral oil.

A recurrent problem for a series of successive voltammetric experiments at the same ZMCPE surface (no mechanical smoothing between measurements) is the existence of memory effects from one analysis to another because of significant solution ingress in the bulk of the electrode. From this point of view, Fig. 3 illustrates the definite advantage of ZMCPEs prepared from solid paraffin over conventional ones containing mineral oil as

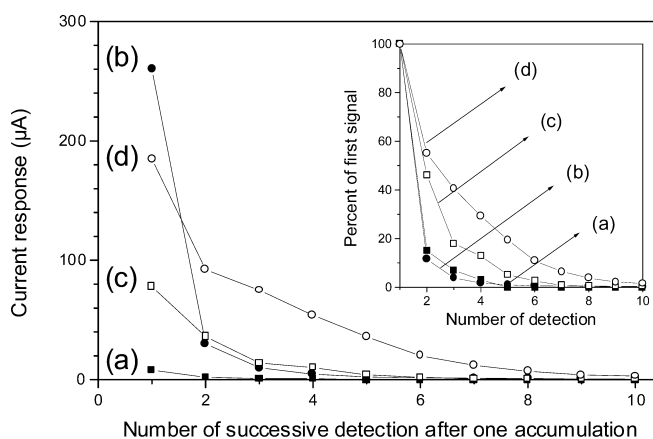


Fig. 3 Peak current response for release of Cu^{2+} from several modified electrodes into 0.1 M KNO_3 , after one open-circuit accumulation from a $0.01 \text{ M Cu(NO}_3)_2$ solution during 30 min. Electrodes were (a) unmodified solid carbon paste, (b) 10% zeolite-modified solid carbon paste, (c) unmodified conventional carbon paste, and (d) 10% zeolite-modified conventional carbon paste. Other conditions as in Fig. 2

a binder, in the example of voltammetric detection of Cu^{2+} species after their accumulation at open circuit during a long time (30 min) from a concentrated solution (2×10^{-2} M), i.e. drastic conditions liable to induce significant memory effects. Clearly, much faster desorption of copper was obtained with the solid ZMCPE, resulting in complete loss of signal after only four detection runs, while the classical ZMCPE still displayed 25% of the initial signal intensity at the same stage. This result indicates that the chemical regeneration of the solid ZMCPE is faster than the classical one and also more quantitative, most probably because of restricted dissolution of the bulk electrode by the external solution in the former case. Memory effects were also studied on unmodified carbon pastes (prolonged accumulation times in concentrated solution gave rise to non-negligible sorption on bare electrodes); once again they were less with the solid carbon paste than with the one based on mineral oil. The release efficiency was even more impressive when decreasing the preconcentration time and the analyte concentration (e.g. 2 min accumulation from a 1×10^{-5} M Cu^{2+} solution led to total desorption during the first detection run with the solid ZMCPE and only 60% loss when using the classical ZMCPE).

Finally, one should mention that performing the anodic stripping step in the differential pulse mode enables copper determination in the submicromolar concentration range, as pointed out in preliminary experiments. As the metrological aspects were not the purpose of the present work, however, no attempt to optimize the analytical protocol was carried out here.

Reproducibility

Figure 4 depicts the results obtained for successive preconcentration analyses of the same Cu^{2+} sample performed at either the solid or the classical ZMCPE without applying any mechanical regeneration treatment to the electrode surface between each measurement. Both electrodes were characterized by similar data dispersion. However, a constant response was observed when using the solid ZMCPE, whereas a slight increase in the electrode sensitivity was noticed when increasing the number of successive measurements at the same surface of the conventional electrode. This increase is due to the progressive ingress of the external solution deeper and deeper into the bulk electrode as the number of experiments increases, owing to the hydrophilic character of zeolite particles. In case of the solid ZMCPE, the ion exchange reactions (accumulation and leaching prior to detection) seem to be limited to those zeolite particles located at the outermost surface of the composite electrode.

Effect of preconcentration time

As common for voltammetric analyses after preconcentration at chemically modified carbon paste electrodes [42], the time afforded to the accumulation to

take place has a significant influence on the current signals. This is illustrated in Fig. 5 for various analyte concentrations. As expected, peak currents increased when lengthening the accumulation time to reach a maximum value corresponding to the maximum zeolite capacity in the corresponding experimental conditions. The maximal value was attained more rapidly by performing preconcentration from more concentrated solutions. To be quantitative with respect to the copper concentration, calibration must be performed in the linear region where peak currents are directly proportional to the preconcentration time, as longer

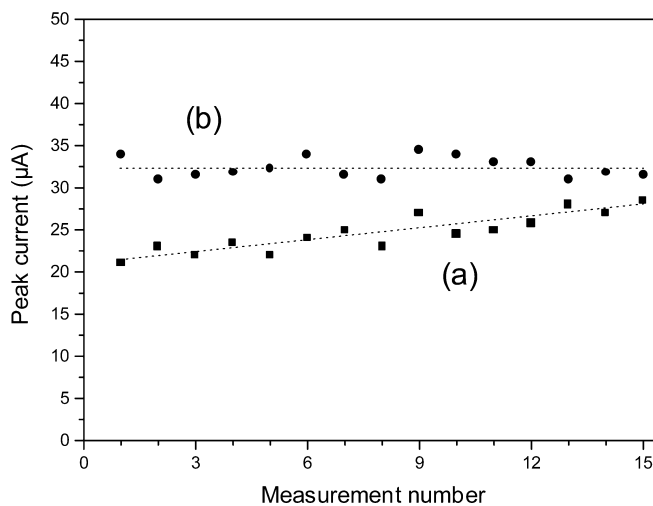


Fig. 4 Peak current response for successive voltammetric analyses of Cu^{2+} , after 2 min open-circuit accumulation from a 2×10^{-4} M $\text{Cu}(\text{NO}_3)_2$ solution, at the same surface of (a) 10% zeolite-modified conventional carbon paste electrode, and (b) 10% zeolite-modified solid carbon paste electrode. Other conditions as in Fig. 2

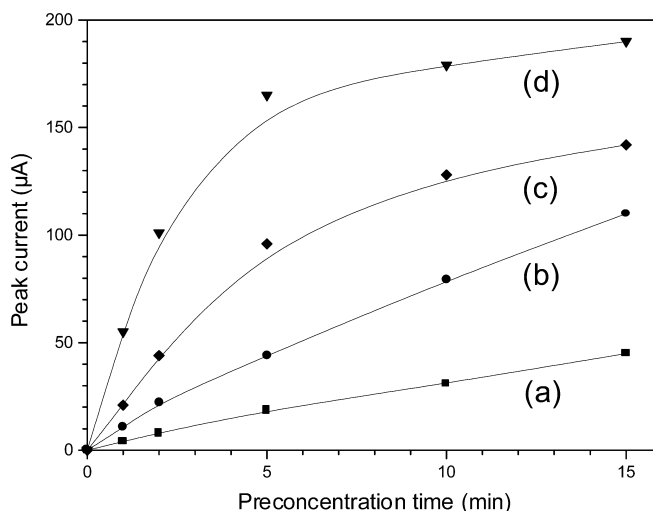


Fig. 5 Influence of the preconcentration time on the peak current response for the voltammetric analysis of various Cu^{2+} samples: (a) 1×10^{-5} M; (b) 5×10^{-5} M; (c) 1×10^{-4} M; and (d) 5×10^{-4} M $\text{Cu}(\text{NO}_3)_2$, at a 10% zeolite-modified solid carbon paste electrode. Other conditions as in Fig. 2

equilibration times gave rise to accumulated quantities rather controlled by the thermodynamics of the ion exchange. No attempt was made here to optimize the electrode preparation to obtain the highest sensitivity.

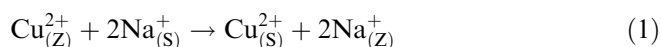
Mechanical stability

Another attractive feature of solid ZMCPEs, which makes them superior to the classical ones, is their better mechanical stability over prolonged use. In addition to their steady voltammetric response, even after several preconcentration steps in stirred media, the mechanical stability of solid ZMCPEs was demonstrated by checking the absence of leaching of zeolite particles into the external solutions. All the different kinds of ZMCPE used in this work (film-based and bulk composites, graphite-based and ketjenblack-containing electrodes) were placed separately in a known volume of aqueous solution that was vigorously stirred with a magnetic bar continuously during 24 h. After this treatment, the electrode was removed, 0.1 M citric acid was added to the medium (to destroy the zeolite structure and release its sodium and aluminum content in solution [11]), and soluble sodium and aluminum species were determined. These concentrations constitute a direct measurement of the zeolite particles that were eventually removed from the electrode surface and dispersed in the solution during the stirring event. The results clearly indicate that no zeolite was lost from zeolite electrodes made of solid carbon paste (only those film-based electrodes that had not undergone thermal treatment resulted in a little leaching), while the conventional ZMCPEs gave rise to significant deterioration of the electrode surface, as otherwise noted by the appearance of graphite particles in suspension.

Indirect amperometric detection and flow injection analysis

Such higher mechanical resistance in a stirred medium would also lead to improved performance in the case of utilization of such an electrode as an amperometric detector in flowing streams, as exemplified hereafter for the detection of non-redox species.

An elegant application of zeolite-modified electrodes in electroanalysis is the indirect amperometric detection of non-electroactive cations [19, 23, 24, 43]. The general principle is based on the use of zeolite particles exchanged with a redox mediator (e.g. Cu^{2+}) that is liberated from the zeolite structure by ion exchange each time a cationic analyte sample (e.g. Na^+) is injected at the zeolite electrode surface (Eq. 1), which is simultaneously reduced (Eq. 2) if applying a suitable cathodic potential at the electrode:



where the subscripts Z and S refer to the zeolite phase and the solution, respectively.

As the amount of Cu^{2+} ions that are leached out of the zeolite particles is directly related to the concentration of the injected Na^+ sample, the resulting current response is indirect with respect to Na^+ species and proportional to the Na^+ concentration. It is now well established that such analysis can be performed continuously in flow injection mode, even in the absence of added electrolyte, with the analyte playing in this case both roles of electrolyte and sensitive species [24, 44].

Figure 6 illustrates the use of the solid carbon paste matrix for such an application in flow injection analysis (FIA). As shown, both the bulk and film-based solid ZMCPEs gave rise to reproducible FIA responses and constant background currents (curves B and C). Peak currents obtained with the bulk electrode were twice as high as for the zeolite film electrode, owing to a larger amount of zeolite at the electrode/solution interface in the former case. On the other hand, a conventional ZMCPE containing mineral oil as the binder displayed less reproducible results due to possible mechanical degradation during the measurements (as illustrated in curve A of Fig. 6, via a baseline change after the 7th FIA peak and subsequent variations in the current responses). This behavior was previously reported for other chemically modified carbon paste electrodes [29, 30] and is clearly due to weaker mechanical resistance of conventional carbon pastes in comparison to the robustness of those based on solid paraffin.

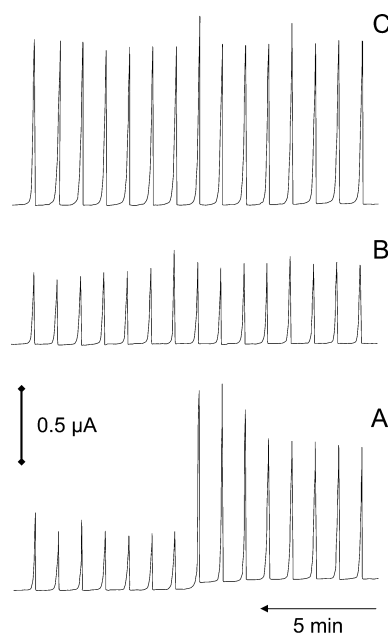


Fig. 6 Relative FIA responses of three Cu^{2+} -doped zeolite modified electrodes to 15 successive injections of Na^+ samples (20 μL of 0.3 mM): **A** zeolite-modified conventional carbon paste electrode; **B** zeolite film on graphite-based solid carbon paste electrode; **C** bulk zeolite-modified solid carbon paste electrode; carrier, deionized water; flow rate, 1 mL min^{-1} ; applied potential, -0.6 V

Conclusions

This work emphasizes the interest of using solid paraffin instead of mineral oil when preparing zeolite-modified carbon paste electrodes. The resulting systems gave rise to less memory effects due to very limited impregnation of the solution in the bulk electrode, as compared to the significant absorption reported for classical ZMCPEs. Moreover, their better mechanical resistance enables prolonged use in stirred media, inducing notably higher performance when applied in FIA. Restricting the presence of zeolite particles only at the electrode surface (film-based ZMCPE) did not improve further the electrode response; the solid ZMCPEs containing zeolite particles dispersed in the whole volume of the bulky composite already display satisfactory characteristics.

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