



Development of an electrochemical sensor based on nanostructured hausmannite-type manganese oxide for detection of sodium ions

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ABSTRACT

The preparation and electrochemical characterization of hausmannite-type manganese oxide to use as a sensing material for sodium ion is described. This paper reports a new *via* synthetic to obtain of the hausmannite-type manganese oxide and its application in the construction of modified electrode as a voltammetric sensor. The electrochemical activity of hausmannite-type manganese oxide is controlled by intercalation/deintercalation of the sodium ions within the oxide lattice. The detection is based on the measurement of anodic current generated by oxidation of $\text{Mn}^{\text{III}}\text{--Mn}^{\text{IV}}$ at electrode surface. The best electrochemical response was obtained for a sensor composition of 20% (w/w) hausmannite oxide in the paste, a TRIS buffer solution of pH 6.0–7.0 and a scan rate of 50 mV s^{-1} . A sensitive linear voltammetric response for sodium ions was obtained in the concentration range of 2.01×10^{-5} – $2.09 \times 10^{-4} \text{ mol L}^{-1}$ with a slope of $355 \mu\text{A L mmol}^{-1}$ and a detection limit of $7.50 \times 10^{-6} \text{ mol L}^{-1}$ using cyclic voltammetry. The use of hausmannite has significantly improved the selectivity of the sensor compared to the birnessite-type manganese oxide modified electrode. Under the working conditions, the proposed method was successfully applied to determination of sodium ions in urine samples.

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1. Introduction

Analysis of alkali metal cations is very important in clinical chemistry, biochemistry and environmental. The determination of blood electrolyte ions (species such as sodium) has been extremely interesting in medicine [1], requiring an analysis easy, fast and reliable. The sodium cation, the main extracellular electrolyte, is responsible for controlling the movement of water between intracellular and extracellular. From the detection of deviation from normal ranges of sodium can be obtained medical information relating to the physical conditions of patients at diagnosis of diseases such as diabetes, renal and hepatic dysfunction, hyponatremia [2,3], heart and hormonal problems [4].

The methods used for determining the sodium cation involved flame photometry [5], spectrophotometric techniques [6–9], electrophoresis and chromatography [10]. In studies using electrochemical techniques, most of the sensors developed in the literature for determination of alkali metal cations are ion-selective electrodes [11–13]. Within this group of sensors, inorganic compounds featuring three-dimensional structures with interstitial

site has been recently proposed in the construction of selective electrodes for alkali metal ions [14,15], which is the case of manganese oxide. The manganese oxides are arranged in various porous structures, which represent a large class of materials formed by octahedral structure of MnO_6 . These crystals are porous materials with great potential and interest for electrode development due to their specific properties and different structures, as well as their applications in adsorption, catalysis [16] and electrochemical sensors [17,18]. In our laboratories, we have developed highly sensitive and selective methods for the determination of non-electroactive ions using electrodes modified with different allotropic forms of manganese oxide [19–25]. Recently, we have studied the preparation and electrochemical characterization of a carbon paste electrode modified with layered birnessite-type manganese oxide for use as a sodium sensor [26]. The detection is based on the measurement of anodic current generated by oxidation of $\text{Mn}^{\text{III}}\text{--Mn}^{\text{IV}}$ at the surface of the electrode and consequently the sodium ions extraction into the birnessite structure.

The hausmannite is a distortion of the spinel structure because of the Jahn-Teller effect for octahedrally coordinated Mn^{III} [27,28]. This polymorph of manganese oxide is a metastable intermediate in the oxidation of Mn^{II} to form insoluble MnO_2 phase, which is thermodynamically stable [29,30]. Materials developed with Mn_3O_4

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have been widely studied theoretically and experimentally in several studies because of its unique electronic configuration and distorted spinel-type structure, associated to its unique properties of ion extraction, molecular adsorption, electrochemical, catalytic and ferromagnetic [31–36].

This paper reports a new *via* synthetic to obtain of the hausmannite-type manganese oxide and its application in the construction of modified electrode as a voltammetric sensor for sodium ion determination. The use of hausmannite has significantly improved the selectivity of the sensor compared to the birnessite-type manganese oxide modified electrode [26].

2. Experimental

2.1. Reagents and solutions

All the solutions were prepared using water purified with a Millipore Milli-Q system. All chemicals used were of analytical high grade and without further purification. The supporting electrolyte used for all experiments was a 0.1 mol L⁻¹ tris(hydroxymethyl)aminomethane (TRIS) buffer solution. A stock solution of 1.00 × 10⁻² mol L⁻¹ sodium ion was prepared daily by dissolving sodium chloride (Aldrich) in 100 mL of 0.1 mol L⁻¹ TRIS buffer solution. Graphite powder (1–2 μm particle size from Aldrich) and mineral oil (Aldrich) of high purity were used for the preparation of the carbon paste.

2.2. Apparatus

The X-ray diffractograms (XRD) were obtained using a Shimadzu model XRD-6000, automated diffractometer with Cu K_{α1} radiation (30 kV and 40 mA) and graphite monochromator at a scan rate of 0.02° min⁻¹ in an interval at 5°–75°. The morphology of the manganese oxide was also characterized by Scanning Electronic Microscopy (SEM), using a Zeiss (DSM 960) microscope.

The voltammetric measurements were conducting a conventional electrochemical cell containing three electrodes: hausmannite-type manganese oxide modified electrode (sodium sensor) as working electrode, a saturated calomel electrode (SCE) as reference electrode and platinum as auxiliary electrode. Cyclic voltammograms were obtained in a potential range between -0.5 V and +1.2 V vs. SCE at 50 mV s⁻¹ in 0.1 mol L⁻¹ TRIS solution (supporting electrolyte) in the absence and presence of sodium ions. These measurements were performed in a potentiostat/galvanostat μ-AUTOLAB type III (Eco Chimie) controlled by a personal computer.

2.3. Hausmannite-type manganese oxide preparation

The hausmannite oxide was synthesized using a modified procedure reported by Feng et al. [37]. Initially, all solutions were treated with N₂ (>99.9%). After, was prepared 200 mL of 0.5 mol L⁻¹ MnCl₂ and 250 mL of 5.5 mol L⁻¹ NaOH. Then, these solutions were again treated with bubbling nitrogen for 20 min. The solution of NaOH was cooled to 0 °C and quickly added to the solution of MnCl₂, which was at a temperature of 10 °C. From this stage, it began to bubble the O₂ from the air (about 20%, flow = 0.58 L min⁻¹) in the mixture for 50 h, keeping the temperature at 20 °C. The stirring of the mixture was 250 rpm. Then the precipitate was filtered and washed with deionized water until filtrate keep pH below 9.0. The remaining solid material was finally dried at 60 °C for 12 h.

The reaction of extraction of sodium ion of the matrix structure hausmannite was obtained by acid treatment. Oxide samples were stirred in 1 mol L⁻¹ nitric acid over different cationic extraction periods (24, 48 and 96 h). The remaining solid material was

washed with deionized water, filtered, and finally dried in air at 60 °C.

2.4. Sensor preparation

The modified carbon paste electrode was prepared manually by carefully mixing the dispersed graphite powder with hausmannite-type manganese oxide at several mass ratios and subsequently adding a fixed quantity of 150 mg of mineral oil (15% w/w). Those mixtures were mixed by magnetic stirring in a 50 mL beaker containing 10 mL of hexane. Thus, the final paste was obtained by the solvent evaporation. After, the modified carbon paste was packed into an electrode body consisting of a plastic cylindrical tube (i.d. 3 mm) equipped with a stainless steel rod serving as an external electric contact. Appropriate surface was achieved by pressing the electrode surface (surface area 12.6 mm²) against a filter paper.

2.5. Urine samples containing sodium ion

The sodium determinations were realized in urine samples without prior treatment. The sample solution was prepared by diluting appropriate aliquots of the urine in the TRIS buffer solution (pH 6.0–7.0) prior to analysis. The sodium ions concentrations of two different human urine samples were determined by cyclic voltammetric using the proposed sodium sensor under the previously optimized experimental conditions. The sodium ions concentration was determined by the standard addition method and compared with the values obtained by atomic absorption spectrophotometry (Atomic Absorption Spectrophotometer SpetrAA 50B – Varian) at a wavelength of 589 nm.

3. Results and discussion

3.1. Hausmannite-type manganese oxide characterization

Structural characterization of hausmannite oxide was performed by XRD, providing a diffractogram (see Fig. 1A), where the confirmation hausmannite phase was performed by comparison with JCPDS File No. 24-0734 (see Fig. 1B).

Crystalline reflection peaks of greater intensity, which located at 2θ = 32.45° and 36.14° representing a distance of 0.277 and 0.249 nm, respectively. The other peaks located at 2θ = 59.41°, 29.11°, 58.47°, 18.11°, 31.0°, 38.14°, 44.56°, 49.77°, 50.88°, 53.88°, 56.07°, 64.62° and 74.10° are also characteristic of three-dimensional structure and the distorted Mn₃O₄. The mean size of the crystallites (d) of this phase was calculated utilizing the equation of Scherrer [38]:

$$d = \frac{k \cdot \lambda}{\beta \cos \theta} \quad (1)$$

where *k* is the proportionality constant which depends on the shape of the particles, assumed as being spherical (0.9 or 1.0), *λ* the wavelength of the radiation of CuK_α (1.5406 Å) and *β* the width at peak half-height. The mean size of the crystallites, calculated for various (*hkl*), was 690 nm, indicating the formation of material with nanometric dimensions.

Hausmannite contains both manganous and manganic ions, belongs to class of mixed valence compounds, in which there is feeble interaction between different ion sites. In general, Mn₃O₄ contains the mixed valence states of Mn^{II} and Mn^{III} which can be represented as MnO·Mn₂O₃. However, some researchers [39,40] have suggested the presence another possible oxide compositions 2MnO·MnO₂ (with Mn^{II} and Mn^{IV}). Several possible distributions of Mn^{II}, Mn^{III} or Mn^{IV} in either the tetragonal or the octahedral sites of the spinel lattice have been proposed [41,42]. Also, more

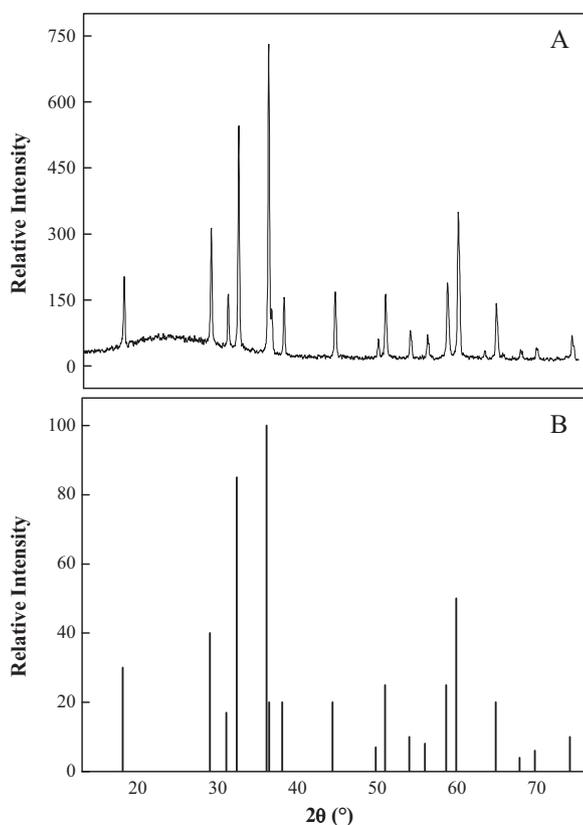


Fig. 1. The XRD patterns of (A) hausmannite-type manganese oxide synthesized and (B) JCPDS File number 24–0734.

recent determinations by XRD spectrum could not bring conclusive evidence either on the speciation or on the partition of the species at the surface. Fig. 2A e 2B illustrates typical SEM micrographs obtained for the hausmannite-type manganese oxide at two different magnifications of 10,000× and 60,000×, where grains of similar forms and uniform size distribution were observed.

3.2. Electrochemical behavior of the sodium sensor

Cyclic voltammograms of hausmannite-type manganese oxide modified electrode were obtained in 0.1 mol L⁻¹ Tris buffer (pH = 8.0) in the absence (curve A – Fig. 3) and in the presence of 3.98 × 10⁻⁵ mol L⁻¹ of sodium ions (curve B – Fig. 3). In this study, the hausmannite-type manganese oxide treated with 1.0 mol L⁻¹ nitric acid for 48 h for removal of sodium ions present in the oxide matrix was used as active material in the construction of the sensor.

The cyclic voltammogram of the sensor registered in the presence of sodium ions in TRIS buffer solution reflecting the electroactivity of hausmannite-type manganese oxide for sodium ions (see curve B – Fig. 3). The peak potential separation ($\Delta E_p = E_{pa} - E_{pc}$) was of 0.39 V for potential scan rate of 50 mV s⁻¹ indicating that the redox process is a quasi-reversible system. The anodic peak ($E_{pa} = 0.45$ V vs. SCE) and cathodic peak ($E_{pc} = 0.06$ V vs. SCE), can be ascribed to electrochemical response of the Mn^{III}/Mn^{IV} redox couple with insertion/extraction of sodium ion. The electrochemical activity of hausmannite-type manganese oxide is controlled by intercalation/deintercalation of the alkali metal cations (Na⁺) within the oxide lattice [43–45]. This electrochemical activity can be represented by equations:

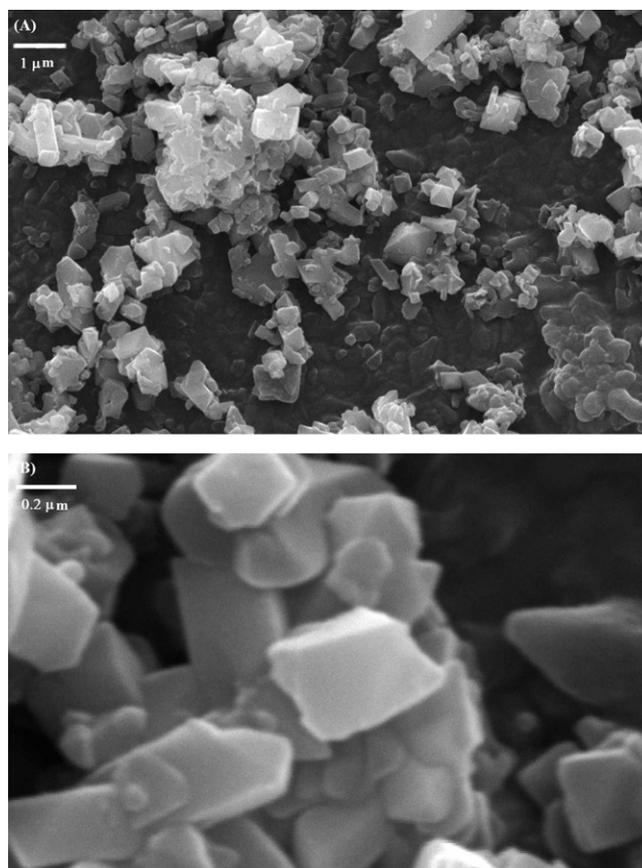
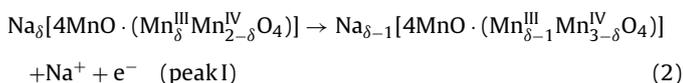
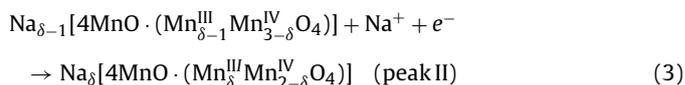


Fig. 2. SEM images of hausmannite-type manganese oxide. (A) 10,000× and (B) 60,000×.



where $2 \leq \delta \leq 1$ and, $\text{Na}_{\delta-1}[4\text{MnO} \cdot (\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_{3-\delta}\text{O}_4)]$ and $\text{Na}_\delta[4\text{MnO} \cdot (\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_{2-\delta}\text{O}_4)]$ stand for the oxy manganese species under the higher and lower oxidation states, respectively. The linear relations were obtained with peak currents vs. the square root of the scan rate revealing an electronic transfer controlled by diffusion (Supplementary data). These results allow concluding that the charge transfer reaction of Mn^{IV}/Mn^{III} is controlled by diffusion of sodium ions in the solid phase. Teixeira et al.

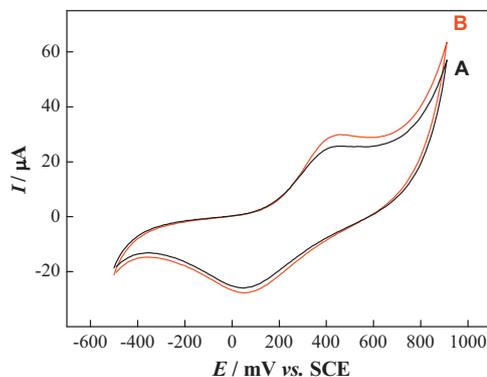


Fig. 3. Cyclic voltammograms at a scan rate of 50 mV s⁻¹ for the sodium sensor in TRIS buffer solution in the (A) absence of sodium ions and in the (B) presence of 3.98 × 10⁻⁵ mol L⁻¹ sodium ions.

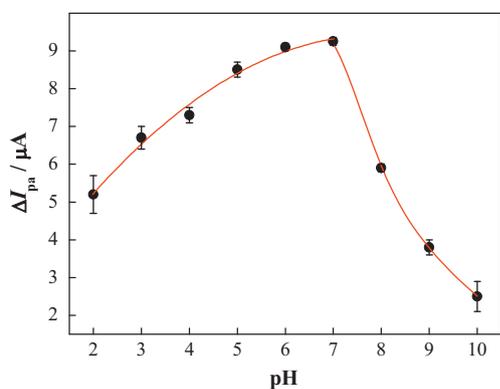


Fig. 4. pH dependence on electrochemical response of the sodium sensor in TRIS buffer solution containing $3.98 \times 10^{-5} \text{ mol L}^{-1}$ sodium ions. The anodic peak current (ΔI_{pa}) was obtained from difference of the current values in the absence and presence of sodium ions.

[24] developed a carbon paste electrode modified with spinel manganese oxide for determination of lithium ions and reported that the electrochemical insertion of cation into the structure in the oxide consists of three processes: solution mass transport, dehydration and transfer at the solid surface and solid-state diffusion. In the absence of sodium ions (curve A – Fig. 3), the cyclic voltammogram of the sensor showed the same voltammetric profile with a magnitude of current lower than in the presence of sodium ion in solution. Hence, the presence of the redox couple in the absence of sodium ions in solution indicates vestige of the intercalation of sodium ions in the hausmannite structure that occurred during its preparation. However, the sodium vestige is required to start the activity of the electrode.

The effect of paste composition on the voltammetric response of the sodium sensor was initially evaluated in 0.1 mol L^{-1} TRIS buffer (pH 8.0) containing $3.98 \times 10^{-5} \text{ mol L}^{-1}$ of sodium ion. Cyclic voltammograms (see Supplementary data) were obtained with the hausmannite-type manganese oxide modified electrode in different oxide proportions (0–30% w/w), where the peak currents increased according to the elevation on amount of hausmannite-type manganese oxide. Thus, the amount of hausmannite in the carbon paste had a significant influence on the voltammetric response. For amounts of manganese oxide greater than 25% (w/w), the voltammetric profile was considerably different exhibiting a distortion of the cyclic voltammogram, which can be ascribed to decrease of the graphite content in the paste, thus reduces the conductive area at the electrode surface. The increase of the ohmic resistance of the electrode makes it unsuitable for analytical applications due to a significant change in the capacitive current and a pronounced decrease in the electron-transfer rate at the electrode [46,47]. This way, the best carbon paste composition was found to be an electrode composition of 20% (w/w) hausmannite-type manganese oxide, 65% (w/w) graphite and 15% (w/w) mineral oil.

The influence of the pH on the electrochemical response of the sodium sensor was studied over a pH range at 2.0–10.0, controlled with TRIS buffer in the absence and presence of sodium ions ($3.98 \times 10^{-5} \text{ mol L}^{-1}$). The cyclic voltammograms of the sodium sensor were performed in the potential range from -0.6 to $+1.0 \text{ V vs. SCE}$ at a scan rate of 50 mV s^{-1} in different pHs. The results obtained indicated that the current values of anodic peaks are strongly influenced by pH and reached a maximum value at $\text{pH} \sim 7$, as shown in Fig. 4. The values of anodic current ($\Delta I / \mu A$) were obtained by difference of the current values in the presence and absence of sodium ions for each pH studied.

The results indicate that at low pH values occurs decrease in the magnitude of peak current in the sensor. This behavior was

Table 1

Effect of the extraction of sodium ions from hausmannite-type manganese oxide in the anodic peak current (ΔI_{pa})^a of the sodium ion sensor.

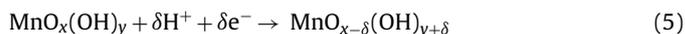
Cationic extraction periods	$\Delta I_{pa} (\mu A)$
24 h	15.2
48 h	31.9
72 h	42.8

^a The values of anodic current were obtained by difference of the current values in the presence and absence of sodium ion in solution.

associated to the reaction of disproportionation of Mn^{III} in the matrix of the manganese oxide when the sensor is cathodically polarized Eq. (4). Consequently the disproportionation provides a reduced amount of oxide on the surface of modified electrode, thus a decrease in current in the presence of sodium ions was observed.



Recently, Kozhina et al. [48] studied the electrochemical reductive dissolution of hausmannite-type manganese oxide at carbon paste electrode in 1 mol L^{-1} HCl. The researchers observed that the electrochemical reduction during polarization of the Mn_3O_4 electrode at a constantly varying potential is determined by the potential scan direction (anodic or cathodic scan). At pH values above 7, there was a marked decrease in current variation as a consequence of Mn^{III} ions form complex oxide soluble in strongly alkaline solution. Kenzie [49] describe that hausmannite, manganite, and others lower oxides are rapidly oxidized under alkaline conditions and consequently deintercalation of the metal cations within the oxide lattice. The peak potentials of the modified electrode hardly changed at pH 3–7, meaning that the voltammetric behavior of the sodium sensor does not involve a proton transfer process but simply a single electron transfer process under the experimental conditions. However, the redox potential was pH dependent in the range 7.0–9.0 with a linear slope value of -0.044 V pH^{-1} , which was ascribed to a one-proton/one-electron transfer process. According to previous reports [50–52], the slope observed occurs due to structural change of Mn_3O_4 which can be described as:



Effects of extraction time on the extraction yield of sodium ions in the hausmannite oxide were carried out under different times by acid treatment. The hausmannite samples were treated with HNO_3 1.0 mol L^{-1} over different cationic extraction periods (24, 48 and 72 h) and evaluated in the carbon paste electrode in 0.1 mol L^{-1} Tris buffer (pH 6.0–7.0) in the absence and presence of sodium ions ($3.98 \times 10^{-5} \text{ mol L}^{-1}$) by cyclic voltammetry. The higher variation in the anodic peak current was obtained with hausmannite sample that was subjected to 72 h of sodium ion extraction (see Table 1). However, the cyclic voltammogram of the sample subjected to 48 h of cationic extraction presented the best voltammetric profile, and this oxide was used for all further studies.

3.3. Analytical performance of the sodium sensor

The influence of alkaline (Li^+ , K^+ , Rb^+), earth alkaline (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) and NH_4^+ ions on the response of the sensor were also studied. Fig. 5(1)–(4) show two studies of the interference effect on electrochemical response of the sodium sensor. In the first study (Fig. 5(1) and (2)) the voltammetric measurements were performed in individual solutions of each interferent cation. In the second study (Fig. 5(3) and (4)) the voltammetric measurements were performed in the interferent solution containing sodium ions in the same concentration. Fig. 5 shows the effect of these different cations in the voltammetric response of the sensor, where the

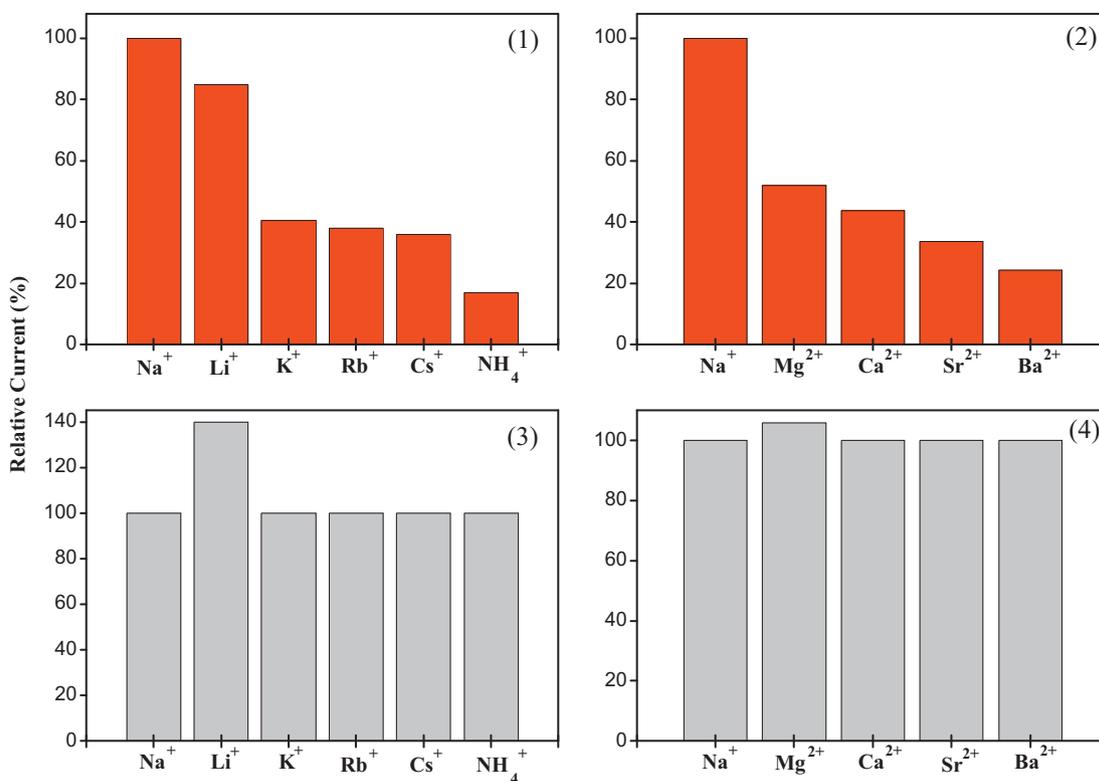


Fig. 5. Interference dependence on electrochemical responses of the sodium sensor in TRIS buffer solution containing $3.98 \times 10^{-5} \text{ mol L}^{-1}$ of Na^+ , Li^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} ions. (1) and (2) = interference cation in absence of ion sodium. (3) and (4) = interference cation in presence of ion sodium ($3.98 \times 10^{-5} \text{ mol L}^{-1}$). Relative current = (current signal of the cation/current signal of the sodium) \times 100%.

relative current (%) was calculated by peak current ratio of the interference cation to the sodium ion, *i.e.* (current signal of the cation/current signal of the sodium) \times 100%.

As a result, the selectivity sequences can be related to the pore size of the manganese oxide. Thus, the selectivity sequences are $\text{NH}_4^+ < \text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Li}^+ < \text{Na}^+$ and $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Na}^+$ for sodium sensor. The weaker responses to earth alkaline ions than to alkaline ions having similar ionic radius may be ascribed to their higher energies of dehydration which is needed for uptake of cations into the solid phase from the aqueous solution. On the other hand, when electrochemical measurements were recorded in interferent solutions containing sodium ions in the same concentration, a significant increase in the relative currents was not observed, indicating that the insertion reaction occurs preferably for sodium ions. Among these tested metallic cations, lithium ion caused a positive interference in the sensor response that was ascribed to ionic radius smaller than a sodium ionic radius. This way, the reactions of intercalation/deintercalation of the lithium within the hausmannite structure can occur.

The dependence of anodic peak current of the sodium sensor with the pre-concentration was investigated. The voltammetric responses of the sensor were realized in the absence and presence of $3.98 \times 10^{-5} \text{ mol L}^{-1}$ of sodium ions in 0.1 mol L^{-1} TRIS buffer (pH 6.0–7.0) after pre-concentration at 0.0 V vs. SCE for different times. The difference of the anodic peak currents in the presence and absence of sodium ions increases with the increasing of the pre-concentration time between 0 and 80 s. It has become nearly constant due to the surface saturation of the oxide with sodium ion. Based on this experiment, it is demonstrated the ability of the sodium to accommodate non-electroactive cation and promote the electroactivity in function of the intercalation sodium in the hausmannite structure. Hence, for all subsequent measurements, a pre-concentration time of 80 s was employed.

The analytical curve for different sodium concentration was obtained from the sensor in the best conditions. The cyclic voltammograms for sodium determination was realized with addition of sodium ion dissolved in 0.1 mol L^{-1} TRIS buffer (pH 6.0–7.0), where the analytical curve was obtained by the anodic peak current in function of sodium concentration (Fig. 6) with $I_{\text{pa}} (\mu\text{A}) = 19.5 + 355 [\text{sodium} (\text{mmol L}^{-1})]$ ($n = 11$; $r = 0.9994$) equation for concentration range at 2.01×10^{-5} to $2.09 \times 10^{-4} \text{ mol L}^{-1} \text{ Na}^+$ and $7.50 \times 10^{-6} \text{ mol L}^{-1}$ of detection limit.

3.4. Determination of sodium ions in urine samples

The sodium ions concentrations of three different human urine samples were determined by cyclic voltammetric using the proposed sodium sensor under the previously optimized experimental

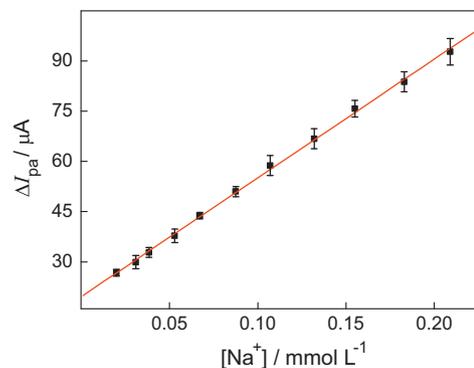


Fig. 6. Analytical curve for sodium ions in 0.1 mol L^{-1} TRIS buffer solution (pH 7.0) using the sodium sensor with a pre-concentration time at 0.0 V vs. SCE at 80 s. Scan rate = 50 mV s^{-1} .

Table 2

Comparative results for the determination of sodium ions ($n=3$) content in urine samples using the voltammetric methodology and atomic absorption spectrophotometry.

Samples	Sodium ions (meq L ⁻¹)		E_r (%) ^a
	Spectrophotometry	Voltammetry	
1	39.9 ± 0.1	40.1 ± 0.1	0.5
2	32.8 ± 0.2	32.8 ± 0.2	0

^a E_r = relative error, voltammetric method vs. spectrophotometric method.

Table 3

Results of addition–recovery experiments using voltammetric procedure for three different standard concentrations of sodium ion.

Sodium ion ^a (μmol L ⁻¹)		Recovery (%)
Added	Found	
38.5	37.2	96.6
67.2	68.1	101
107	110	103
132	132	100

^a $n=3$.

conditions. The sodium determinations were realized in urine samples without prior treatment. The sodium ions concentration was determined by the standard addition method and compared with the values obtained by atomic absorption spectrophotometry at a wavelength of 589 nm. Relevant analyses are summarized in Table 2. The statistical calculations for the assay results show significant precision for the proposed sensor.

In the addition and recovery study, four different sodium concentrations (38.5, 67.2, 107 and 132 μmol L⁻¹) were added in triplicate in the urine sample (Table 3). Recoveries between 96.6% and 103% of sodium ion were obtained using the proposed sensor; it suggests the absence the interference of matrix effect in the procedure.

4. Conclusions

The present study demonstrates that the hausmannite-type manganese oxide can be used as a sensing material for sodium ion. The electrochemical behavior of the sodium sensor was well defined and stable. The best electrochemical response was obtained for an electrode composition of 20% (w/w) hausmannite-type manganese oxide in the paste, a 0.1 mol L⁻¹ TRIS buffer solution at a pH of 6.0–7.0, a scan rate of 50 mV s⁻¹, in accumulation potential of 0.0 V vs. SCE at 80 s pre-concentration time. Under these experimental conditions, the proposed methodology responds to sodium ions in the concentration range of 2.01×10^{-5} – 2.09×10^{-4} mol L⁻¹, with 7.50×10^{-5} mol L⁻¹ of detection limit. The lifetime of the proposed sensor was at least six months, and more than 300 voltammetric measurements were performed using the same electrode surface. The hausmannite is very stable in comparison to spinel manganese oxide [16]. The pure spinel oxide presents a Jahn–Teller distortion resulting in a distortion in the crystalline structure and affecting strongly the stability of the material after successive potential scans.

The lithium ions showed positive interference in the voltammetric response of the sensor. However, the other investigated cations (K⁺, Rb⁺, Cs⁺, NH₄⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺) showed no significant interference in the electrochemical response of the proposed sensor. The sensor has significantly improved the selectivity for sodium when compared to our recent publication [26]. In that work we reported the interference of magnesium ion in the voltammetric response and the need for pretreatment of the sample for elimination of the interferent ion.

The determination of sodium ions in urine using the proposed procedure is characterized by the precision and selectivity. This makes the procedure applicable for the analysis and quality control of clinical samples. According to the *t*-test, there were no significant differences between the calculated and comparative values at an agreement at the 95% confidence level and within an acceptable range of error, indicating that the sodium sensor can be utilized for determination of sodium in urine.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2013.01.030>.

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