



# Electrochemical evaluation of the a carbon-paste electrode modified with spinel manganese(IV) oxide under flow conditions for amperometric determination of lithium

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## ABSTRACT

The participation of cations in redox reactions of manganese oxides provides an opportunity for development of chemical sensors for non-electroactive ions. This paper describes the amperometric determination of lithium ions using carbon-paste electrode modified with spinel manganese(IV) oxide under flow conditions. Systematic investigations were made to optimize the experimental parameters for lithium sensor by flow injection analysis. The detection was based on the measurement of anodic current generated by oxidation of Mn(III) to Mn(IV) at the surface of the electrode and consequently the lithium ions extraction into the spinel structure. An operating potential of 0.50 V (vs. Ag/AgCl/3 KCl mol/L) was exploited for amperometric monitoring. The amperometric signal was linearly dependent on the lithium ions concentration over the range  $4.0 \times 10^{-5}$  to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>. The equilibrium constant of insertion/extraction of the lithium ion in the spinel structure, apparent Gibbs energy of insertion, and surface coverage of the electrode with manganese oxide, were calculated by peak charge (*Q*) in different concentration under flow conditions. Considering selectivity, the peak charge of the sensor was found to be linearly dependent on the ionic radius of the alkaline and earth-alkaline cations.

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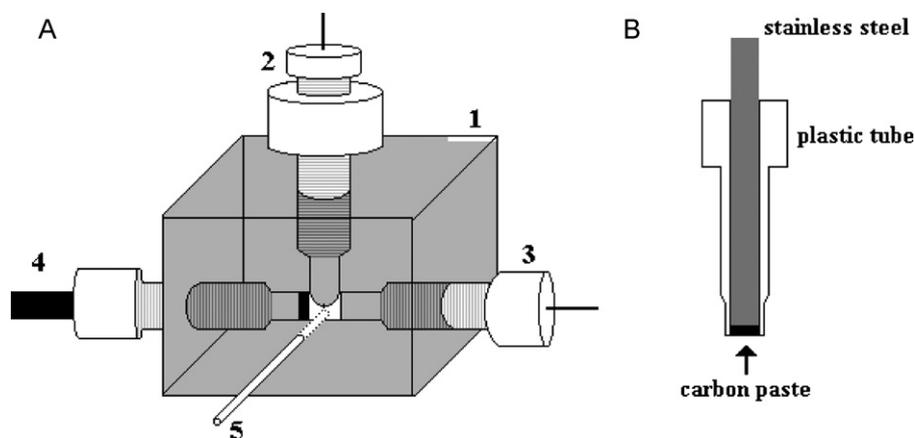
## 1. Introduction

Recently, it has been demonstrated that electrodes modified with metal hexacyanoferrates can be used as sensors for non-electroactive cations. According to Karyakin [1], the first analytical applications of metal hexacyanoferrates based on the topotactic electrochemical reaction of insertion/extraction non-electroactive ions were for thallium, cesium and potassium. However, some cations similarly promote the electroactivity of metal hexacyanoferrate, which affects the selectivity of the corresponding sensors. Karyakin [1] has introduced a comprehensive review about sensors development for non-electroactive ions based on the electrochemical behaviour of metal hexacyanoferrate.

In literature, exist descriptions of others compound with ability of accommodate non-electroactive cations and promote the elec-

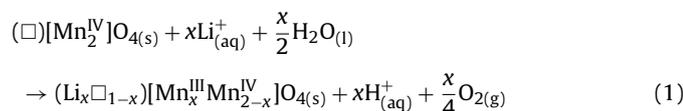
troactivity in function of the insertion cation, among these we may mention the manganese oxide. Manganese oxides represent a large class of materials that have layered and tunneled structures consisting of edge-shared MnO<sub>6</sub> octahedral units. They have attracted considerable interest due to broad potential applications in heterogeneous catalysis, chemical sensing, toxic wastewater treatment, and rechargeable battery technology [2,3]. The manganese oxides have distinct advantages over other materials for applications because of mixed valencies of the manganese ion (mainly 4+, 3+ and 2+). In particular, manganese oxides presenting the spinel structure have attracted much interest as molecular sieves, battery materials, catalysts for the oxidation–reduction process and chemical sensing [4]. The spinel structure shows a three-dimensional (1 × 3) network tunnel connecting 8a tetrahedral sites and empty 16c octahedral sites of a cubic closed-packed oxygen framework [5]. The spinel manganese oxide shows selective adsorptive properties for lithium ions and protons. Several other literature reports have proposed the mechanism of insertion/extraction of lithium ions in spinel-structured manganese oxide [6,7]. Ooi et al. [8] have proposed a redox mechanism for the insertion of lithium ions in the spinel

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**Fig. 1.** Schematic diagram of the electrochemical flow cell used in the amperometric measurements in flow injection system. (A) 1: polyurethane resin block; 2: reference electrode (Ag/AgCl); 3: platinum electrode; 4: carbon-paste electrode modified; 5: polyethylene tubing (flow). (B) Carbon-paste packed into an electrode body.

manganese oxide:



where  $(\square)$ ,  $[\ ]$  and  $\square$  are 8a tetrahedral sites, 16d tetrahedral and vacant sites, respectively. The insertion reaction of lithium ions in the manganese oxide is topotactic in which the reduction of  $\text{Mn}^{\text{IV}}$  to  $\text{Mn}^{\text{III}}$  occurs in the structure and  $\text{O}_2$  gas evolution to maintain the electroneutrality of the spinel. In the previous papers [9–11], our group has reported the applicability of the electrode modified with spinel manganese oxide for the determination of lithium ions by voltammetric measurements.

Several ion-selective electrodes with polymeric membranes containing ionophores (such as diamides, crown ethers, derivatives of natural polyether antibiotics, heteroaromatic compounds and polypropoxylates) were previously reported for the determination of lithium ions [12,13]. However, the amperometric determination of lithium ions in a flow injection system has rarely been investigated. A voltammetric ion-selective electrode based on the facilitated transfer of lithium ions by dibenzyl-14-crown-4 at the *o*-nitrophenyl phenyl ether/water interface was applied by Sawada et al. [14] to the amperometric detector in a flow analysis system with cation-exchange column.

In the present paper we focus in examination of the electrochemical behaviour of carbon-paste electrode modified with spinel manganese oxide using flow injection amperometric procedure for detection of lithium ions. The behaviour of the sensor with respect experimental parameters in flow injection system and its application in the determination of lithium ions are described. We carried out a detailed study of the sensor under flow conditions, obtaining physical-chemical parameters (e.g. equilibrium constant, apparent Gibbs energy of insertion, surface coverage) of the sensor. The amperometric measurements are based on the topotactic electrochemical reaction of insertion/extraction of the non-electroactive cation in the spinel structure.

## 2. Experimental

### 2.1. Materials

All the solutions were prepared using water purified with a Millipore Milli-Q system. All chemicals were of analytical reagent grade and were used without further purification. The supporting electrolyte (mobile phase) used for all experiments was a  $0.1 \text{ mol L}^{-1}$  tris(hydroxymethyl)aminomethane (TRIS) buffer solu-

tion (pH 8.3). A  $0.01 \text{ mol L}^{-1}$  lithium ions solution was prepared daily by dissolving lithium chloride (Merck) in 100 mL of TRIS buffer.

### 2.2. Apparatus

An eight-channel Ismatec (Zurich, Switzerland) model 7618-40 peristaltic pump supplied with Tygar pump tubing was used for the propulsion of the fluids. The manifold was constructed with polyethylene tube (0.8 mm i.d.). The sample injection was performed by three-piece manual injector-commutator, with two fixed side bars and a sliding central bar, which is moved for sampling and injection.

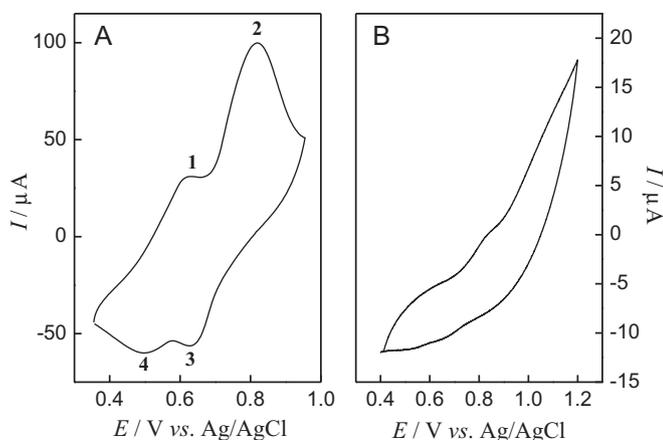
Flow injection amperometric and cyclic voltammetric (CV) measurements were carried out with a microAutolab Type III (Eco Chimie) controlled by personal computer using the GPES 4.9 software. The measurements were performed in a three-electrode flow cell configuration (Fig. 1) using modified electrode ( $0.126 \text{ cm}^2$  area) as working, Ag/AgCl ( $3 \text{ mol L}^{-1}$  KCl) as reference and platinum as auxiliary electrodes ( $\phi = 3 \text{ mm}$  disk). For cyclic voltammetry the potential was varying from 0.4 to 1.1 V (vs. Ag/AgCl) at scan rate of  $50 \text{ mV s}^{-1}$ , stationary solutions were used in such case. The amperometric measurements were performed in flow injection system using the GPES software (Eco Chimie) by chronoamperometry (constant potential). The body of the electrochemical flow cell (Fig. 1A) was made with polyurethane resin from vegetable oil [15] with an effective volume of  $77 \mu\text{L}$ .

### 2.3. Spinel manganese oxide preparation

The spinel  $\text{LiMn}_2\text{O}_4$  was prepared by heat-drying a mixture of electrolytic  $\text{MnO}_2$  and  $\text{LiOH}$  with molar ratio 2:1.05 (Mn/Li) [16]. The resulting mixture was extensively ground and calcined in static air at  $750^\circ\text{C}$  for 24 h. Next, the product was quenched at room temperature in desiccator and ground again. For conversion to spinel manganese oxide, the sample of  $\text{LiMn}_2\text{O}_4$  was suspended in aqueous diluted sulfuric acid solution kept under constant stirring during 45 min. When the pH of this mixture was stabilized at a particular value, the solution was decanted. The remaining solid material was washed with deionized water, filtered, and finally dried in air at  $90^\circ\text{C}$ .

### 2.4. Sensor preparation

As described elsewhere [9], the modified carbon-paste electrode was prepared by carefully mixing 50% ( $m/m$ ) of graphite powder ( $1\text{--}2 \mu\text{m}$  particle size—Aldrich), 25% ( $m/m$ ) spinel manganese oxide



**Fig. 2.** Cyclic voltammogram at a scan rate of  $10\text{ mV s}^{-1}$  for the CPEM with spinel-type manganese oxide in TRIS buffer solution (pH 8.3) in the presence of  $1.0 \times 10^{-2}\text{ mol L}^{-1}$  lithium ions (plot A) and in the absence of lithium ions (plot B).

and 25% ( $m/m$ ) of mineral oil (Aldrich). This mixture was realized by adding 20 mL of hexane with magnetic stirring until evaporation of the solvent. A part of the mixture was packed into a plastic cylindrical tube (o.d. 7 mm, i.d. 4 mm, Fig. 1(B)) connected to a stainless steel rod, obtained the modified carbon past electrode. Appropriate surface was achieved by pressing the electrode surface (surface area of  $12.6\text{ mm}^2$ ) against a filter paper. Before use, the electrode was activated by cycling of the electrode (scan rate =  $25\text{ mV s}^{-1}$ ) in a  $0.01\text{ mol L}^{-1}$  lithium ions in  $0.1\text{ mol L}^{-1}$  TRIS buffer solution (pH 8.3) by cyclic voltammetry (5 cycles).

### 2.5. Flow injection amperometric determination of lithium ions

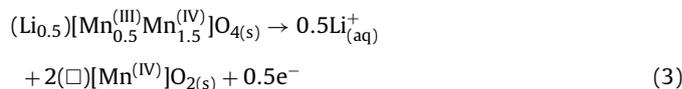
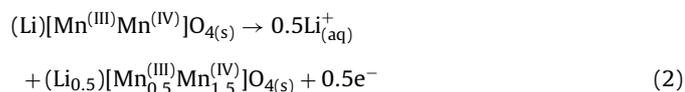
The flow injection amperometric measurements were realized by insertion of the working electrode into a flow injection system [17]. The  $0.1\text{ mol L}^{-1}$  TRIS buffer solution (pH 8.3) was used as mobile phase at a flow rate of  $8.3\text{ mL min}^{-1}$ . The lithium reference in  $0.1\text{ mol L}^{-1}$  TRIS buffer solution contained in the sample volume loop was injected and transported by the mobile phase after the baseline had reached a steady-state value. The analytical path was 30 cm and the entire flow injection system was maintained at room temperature.

## 3. Results and discussion

### 3.1. Cyclic voltammetry studies

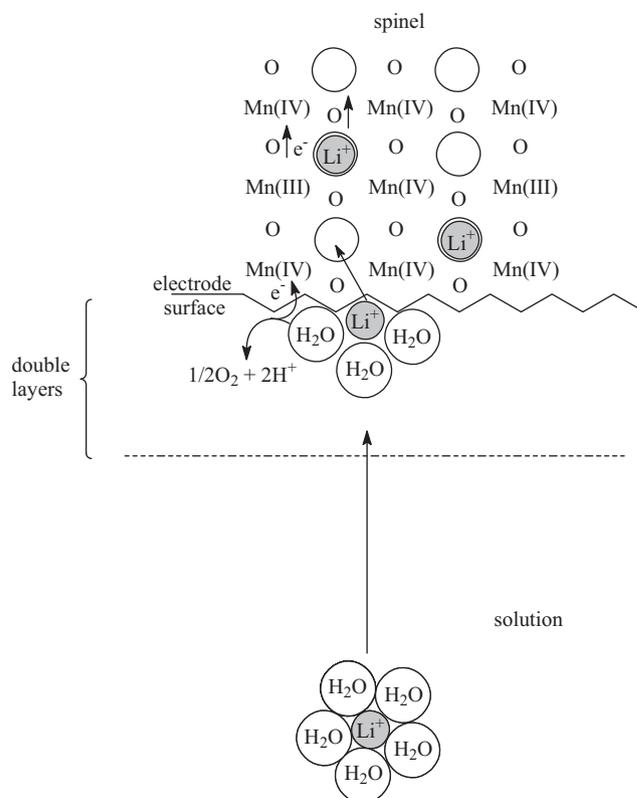
The electrochemical behaviour of the carbon-paste electrode modified (CPEM) with spinel manganese oxide in alkaline media in the presence and in the absence of lithium ions has already been investigated [9–11]. It was shown that in borate buffer (pH 9.0) the modified electrode presented a peculiar electrochemical activity in presence of the non-electroactive cation. Fig. 2A shows a cyclic voltammogram registered in TRIS buffer solution (pH 8.3) containing  $1.0 \times 10^{-2}\text{ mol L}^{-1}$  lithium ions of the CPEM reflecting the electroactivity of spinel manganese oxide for lithium ions.

According to the literature, the region of insertion/extraction of lithium ions in the spinel structure is between 0.4 V and 1.2 V [18]. Cyclic voltammetry shows two peaks on both the anodic and cathodic sides according to the following two electrochemical extraction/insertion reactions [9,18]:



Therefore, the peaks 1 (0.63 V) and 4 (0.50 V) were assigned to the extraction and insertion processes of lithium ions as given by Eq. (2). Moreover, peaks 2 (0.82 V) and 3 (0.62 V) were assigned to the same processes in agreement with the Eq. (3). As described in the literature [19,20], the electrochemical insertion of lithium ions into the structure in the spinel manganese oxide consists of three processes: solution mass transport, dehydration and transfer at the solid surface and solid-state diffusion (Scheme 1). The variation of the peak currents and the peak potential separation ( $\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$ ) of the CPEM with spinel manganese oxide in solution containing  $1.0\text{ mmol L}^{-1}$  lithium ions with scan rate ( $1\text{--}100\text{ mV s}^{-1}$ ) was studied. Linear relations were obtained with peak currents versus the square root of the scan rate revealing an electronic transfer controlled by diffusion. These results allow to conclude that the charge transfer reaction of  $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$  is controlled by diffusion of lithium ions in the solid phase [9]. Hence, the solid-state diffusion of  $\text{Li}^+$  ions can be considered as the rate-determining step. In this study also observed an increase of  $\Delta E_p$  with variation of scan rate, indicating that at high scan rate the redox process becomes kinetically irreversible.

In the absence of lithium ions (Fig. 2B), the voltammetric profile of the CPEM with spinel-type manganese oxide showed a peak in 0.82 V. According to the described experiments, this behaviour could be explained by considering the inserted protons in the oxide structure [20] or vestige of lithium ions in the spinel that occurred during its preparation [16]. According to Hunter's study [21], even after the  $\text{LiMn}_2\text{O}_4$  treatment with sulfuric acid solution (pH 2) was observed 0.5% of residual lithium ions remains in the oxide structure.



**Scheme 1.** Schematic representation of the lithium insertion reaction with spinel-type manganese oxide:  $\circ$  = vacant site.

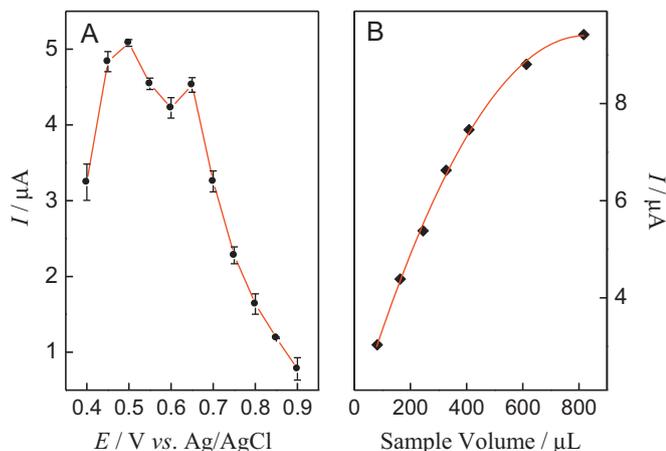
### 3.2. Flow injection amperometric determination of lithium ions

It is necessary to emphasize that before performing FIA measurements, the modified electrode must be conditioned in a TRIS buffer solution (pH 8.3) containing  $0.01 \text{ mol L}^{-1}$  lithium ions by cyclic voltammetry (scan rate =  $10 \text{ mV s}^{-1}$  and potential range =  $0.4\text{--}1.1 \text{ V vs. Ag/AgCl}$ ). This treatment affects directly the hydrodynamic performance of the electrode, increasing the velocity of response in presence of lithium ions in solution.

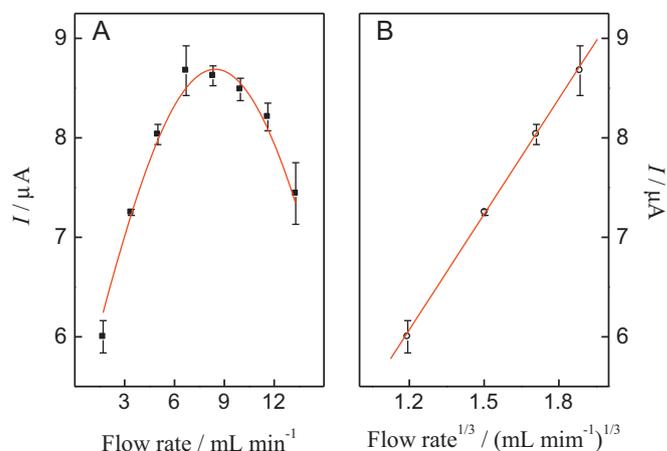
Fig. 3A shows the hydrodynamic voltammogram obtained at the CPEM with spinel manganese oxide for  $81.7 \mu\text{L}$  injections of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  of lithium ions in  $0.1 \text{ mol L}^{-1}$  TRIS buffer solution under various applied working potentials ( $+0.40$  to  $+0.90 \text{ V vs. Ag/AgCl}$ ) for flow rate of  $5.1 \text{ mL min}^{-1}$ . Each data point shown represents the average of at least six injections. The corresponding background voltammogram is also shown. It can be seen that the optimum potential, resulting in the highest response of the sensor for lithium ions, was found to be  $+0.50 \text{ V vs. Ag/AgCl}$ .

The hydrodynamic voltammogram presents two peaks corresponding to the electrochemical extraction of lithium ions into structure in the spinel manganese oxide, similarly with those observed in cyclic voltammetry (see Fig. 2A). This indicates that there are two distinct diffusion processes attributing kinetic aspects of insertion and extraction of ions in the spinel structure. The interaction energy of lithium with surrounding ions varies with the  $\text{Li}^+$  concentration (fractional occupancy in solid or applied voltage), this is the intrinsic reason for varying of the diffusion coefficient. In fact, two types of inserted sites with different energies usually exist in insertion/extraction material for the diffusion and storage of lithium ions. Similar effects have been previously reported for other spinel manganese oxide-modified electrodes and interpreted qualitatively in terms solid-state diffusion coefficients which depend on the degree of insertion [22,23]. The potentials obtained in the hydrodynamic voltammogram are accordingly with half-wave potentials (average value of the cathodic and anodic peaks) of the cyclic voltammetry.

The effect of the sample volume from  $81.7$  to  $817.1 \mu\text{L}$  by changing the length of the sample loop ( $10\text{--}100 \text{ cm}$ ,  $1.02 \text{ mm i.d.}$ ) in the manual injector for a  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  lithium ions in  $0.10 \text{ mol L}^{-1}$  TRIS buffer solution (pH 8.3) on the analytical signal was also investigated. The amperometric response increased with the increase of sample volumes from  $81.7$  to  $817.1 \mu\text{L}$  for flow rate of  $5.1 \text{ mL min}^{-1}$  (Fig. 3B). Therefore, a sample volume of  $408.6 \mu\text{L}$  was selected as a compromise between the conflicting requirements for high sensitivity and sample throughput.



**Fig. 3.** Hydrodynamic responses for lithium ions on the CPEM with spinel-type manganese oxide under flow conditions (plot A) applied working potential and (plot B) sample volume.

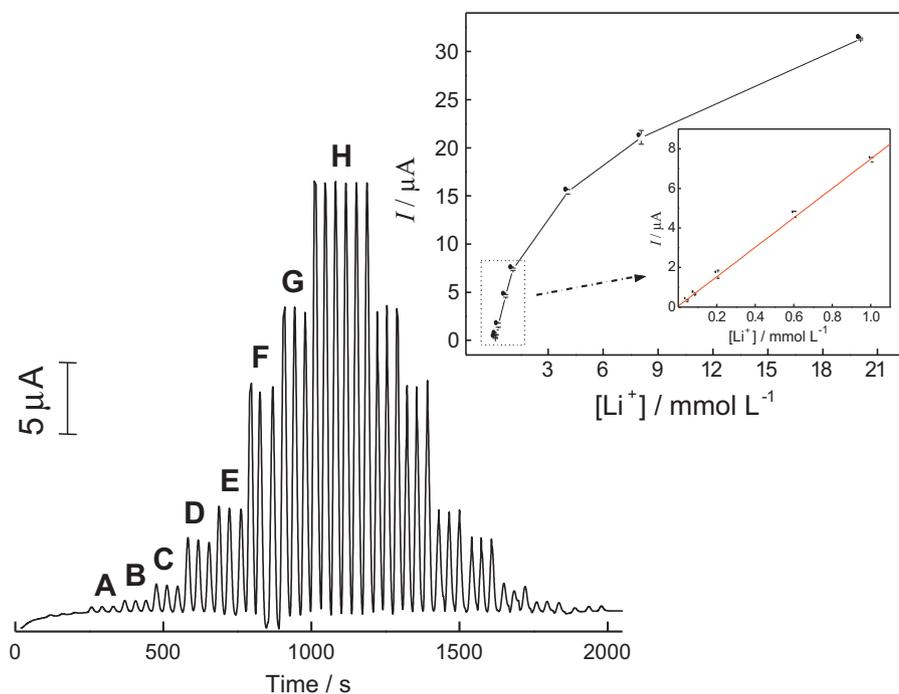


**Fig. 4.** Dependence of flow injection amperometric current on the flow rate (plot A) and correlation of amperometric current on the cube root of flow rate (plot B). Applied working potential =  $+0.50 \text{ V vs. Ag/AgCl}$  and sample volume =  $408.6 \mu\text{L}$  of lithium ion ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ).

The effect of the flow rate on the magnitude of amperometric response was investigated by applying the working potential of  $+0.50 \text{ V vs. Ag/AgCl}$  with sample volume of  $408.6 \mu\text{L}$ . The results showed that the flow injection current response is dependent on the flow rate (see Fig. 4). The current increases with flow rate reaching a maximum value at  $6.7 \text{ mL min}^{-1}$ . Increasing flow rates causes a reduction of the diffusion layer at the electrode surface and consequently an increase of the diffusion current [24,25]. A graph of the amperometric response for lithium ions ( $I_{\text{lim}}$ ) vs. cube root of the flow rate (Fig. 4B) indicated a linear behaviour with a correlation coefficient of 0.9999 in the range flow rate between  $1.7$  and  $6.7 \text{ mL min}^{-1}$  ( $I_{\text{lim}} (\mu\text{A}) = 1.43 + 3.87 [\text{flow rate} (\text{mL min}^{-1})]^{1/3}$ ).

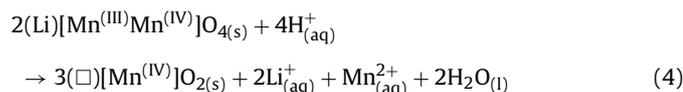
This result is in agreement with previous findings, since the insertion of lithium ions in the oxide structure is relatively a laminar flow regime, which is attained in the thin-layer of electrolyte at the electrode surface. Plot of  $I_{\text{lim}}$  vs. cube root of the flow rate did not extrapolate to zero. The intercept value ( $I_{\text{ind}} = 1.43$ ) corresponds to the axial diffusion of lithium to the electroactive surface independent on the flow rate. The limited electrode response at flow rates higher than  $6.7 \text{ mL min}^{-1}$  may be assigned to the rate-limiting step for charge transfer reaction controlled by diffusion of lithium ions in the solid phase. The diffusion of lithium ions in the spinel manganese oxide becomes the limiting factor at very high flow rates, a decrease in current values should occur as fewer lithium ions are able to penetrate in the solid phase during the shorter residence time of the sample in the cell. A flow rate of  $6.7 \text{ mL min}^{-1}$  was used in the further experiments, which has maintained a good sensitivity and stability of amperometric response. The analytical path (manual injector to electrochemical flow cell) was studied in the range of  $20\text{--}60 \text{ cm}$  under the same experimental conditions as selected before. The results obtained showed that the amperometric response of the CPEM was practically constant in that interval.

The influence of the pH on the amperometric response of the modified electrode was examined over a range of pH 6–11. The current values of the CPEM with spinel-type manganese oxide were carried out with applied potential of  $+0.50 \text{ V vs. Ag/AgCl}$  and sample volume of  $408.6 \mu\text{L}$  ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$  of lithium ions in different pHs 6–11) for a flow rate of  $6.7 \text{ mL min}^{-1}$ . The obtained results indicated that the current values are strongly influenced and reached a maximum value at pH 8.3. At pH under 8.3, occurs the surface disproportionation reaction as proposed by



**Fig. 5.** Transient current signals obtained in triplicate for lithium solutions: (A) 0.040; (B) 0.080; (C) 0.20; (D) 0.60; (E) 1.0; (F) 4.0; (G) 8.0 and (H) 20 mmol L<sup>-1</sup> lithium ion. The inset shows the analytical curve for lithium. Applied working potential = +0.50 V vs. Ag/AgCl; sample volume = 408.6 μL of lithium ion and flow rate = 6.7 mL min<sup>-1</sup>.

Hunter [21]:



could possibly explain such pH dependence on the current values. For pH 9.4 and 10.2, the current values have decreased again probably due to another gradual formation of a surface layer of poorly ordered hausmannite (Mn<sub>3</sub>O<sub>4</sub>) [10,11,26] and consequently blocking the diffusion of lithium ions. The background currents are practically constant in pH range of 6–9. This behaviour demonstrates that the disproportionation reaction occurs in the presence of lithium ions as shown in Eq. (4). However, for pH higher than 9, the increase of the background current values was observed. This performance clearly indicates the formation of the Mn<sub>3</sub>O<sub>4</sub> in surface electrode for high pH values.

After optimizing the best operating conditions for the FIA procedure, amperometric measurements were carried out in TRIS buffer solution (pH 8.3) containing different lithium concentrations in order to obtain the analytical curve. Fig. 5 illustrates the flow current-time response for different lithium concentrations. The current values (at +0.50 V vs. Ag/AgCl) obtained gave a linear relationship with the lithium concentrations from  $4.0 \times 10^{-5}$  to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> (see inside Fig. 6). This plot could be represented by the equation  $(I/\mu\text{A}) = 0.102 + 7487.4 [\text{lithium} (\text{mmol L}^{-1})]$  with correlation coefficient of 0.9998 ( $n = 5$ ).

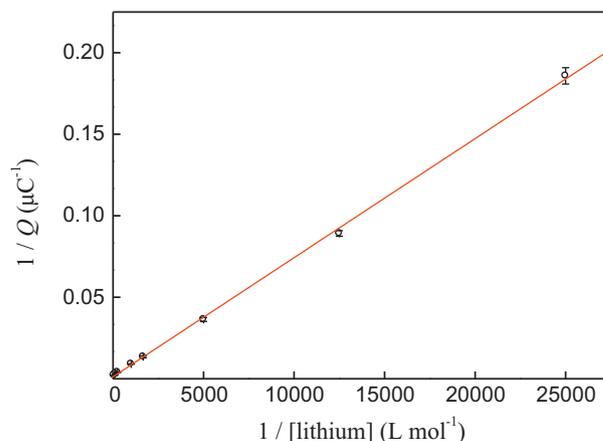
Concentrations above  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> causes a deviation of response linearity that can be explained by the variable insertion of lithium ions and the subsequent saturation of the tunnels of the manganese oxide on the electrode surface. The equilibrium constant of insertion and extraction of the lithium ions in the spinel structure under constant potential and hydrodynamic conditions was calculated from the isotherm data using Langmuir model. A linearized form of the Langmuir model in terms of the lithium concentration ( $C$ ), the accumulated charge at the electrode surface ( $Q$ )

and the saturated charge ( $Q_{\text{sat}}$ ), is given by equation:

$$\frac{1}{Q} = \frac{1}{Q_{\text{sat}}} + \left( \frac{1}{KQ_{\text{sat}}} \right) \frac{1}{C} \quad (5)$$

where  $K$  is equilibrium constant of insertion/extraction of the lithium ion in the spinel structure. The charge for each injected concentration was obtained by area of any current-time peak ( $Q = \int_0^{\infty} I(t)dt$ ). The peak area is independent of the extent of dispersion of the sample and retention time [27]. The amperometric data in Fig. 5 were fitted to Eq. (5), and a linear relation was obtained between  $1/Q$  and  $1/[\text{lithium}]$  (see Fig. 6), getting  $K = 168.4 \text{ L mol}^{-1}$  and  $Q_{\text{sat}} = 813.0 \mu\text{C}$  values. The surface coverage –  $\Gamma$  (mol cm<sup>-2</sup>) of the electrode with spinel-type manganese oxide can be estimated from the relation  $\Gamma = Q_{\text{sat}}/nFA$ , using the saturated charge obtained by Fig. 6. The surface coverage found was  $6.9 \times 10^{-8}$  mol cm<sup>-2</sup>.

Further, the parameter  $K$ , which reflects the affinity of lithium towards insertion sites at constant temperature and electrode



**Fig. 6.** Linearized Langmuir isotherm of lithium ion at the CPEM with spinel-type manganese oxide in TRIS buffer solution (pH 8.3) at 25 °C obtained by means of coulometric data.

potential, can be presented as [28–30]:

$$K = \frac{1}{c_{\text{solvent}}} \exp\left(\frac{-\Delta G_i}{RT}\right) \quad (6)$$

where  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is the gas constant,  $T$  (K) is the temperature,  $\Delta G_i$  ( $\text{J mol}^{-1}$ ) is the Gibbs energy of insertion, and  $c_{\text{solvent}}$  the molar concentration of the solvent, which is for this case water ( $c_{\text{water}} = 55.5 \text{ mol L}^{-1}$ ). Using this equation, the apparent Gibbs energy of insertion of lithium ion onto the spinel structure was calculated from the equilibrium constant data presented in Fig. 6. The mean value obtained in the whole double-layer potential region is  $\Delta G_i = -23.0 \pm 0.4 \text{ J mol}^{-1}$  ( $T = 298 \text{ K}$ ). Also, a high negative Gibbs energy value indicates that the equilibrium for the process lies in favor of insertion of lithium onto the spinel structure.

The influence of alkaline ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ ) and earth-alkaline ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) ions in the response of the carbon-paste electrode modified with spinel manganese oxide has been studied. For this study, the current values of the CPEM were obtained by injection of sample volumes containing  $6.0 \times 10^{-4} \text{ mol L}^{-1}$  of alkaline and earth-alkaline ions in the absence and presence of lithium ions ( $6.0 \times 10^{-4} \text{ mol L}^{-1}$ ). Table 1 shows the relative current (%) which was calculated by difference of the currents in the presence and absence of the cations.

The amperometric measurements realized in the lithium ions absence in solution, exhibit linear dependency with ionic radius size of cation in solution. This feature can be explained on the basis of the ion-sieve effect of the tunnel sites in the spinel structure. In this study was observed a decrease of the relative current with increase ionic radius of the alkaline metal ions ( $\text{Na}^+ > \text{K}^+ > \text{Cs}^+$ ). The same behaviour is observed for earth-alkaline metal ions ( $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ ), but the amplitude currents were greater than alkaline ions. The observed difference in the relative currents may be assigned to the high charge density (ion charge/ionic radius) of the earth-alkaline metal ions; for comparison, the charge density of the alkaline metal ions. Fig. 7 shows the peak charge ( $Q$ ) at the electrode surface vs. ionic radius of the alkaline and earth-alkaline metal ions. The insertion reaction of the ion is subject to the steric effect dictated by the size of the three-dimensional tunnels ( $0.7 \text{ \AA}$ ). As already noted, charge density (charge nuclear ion/ionic radius), ionic size and the lattice spacing on the surface of manganese oxide are important factors in the electrochemical insertion phenomenon [31–33].

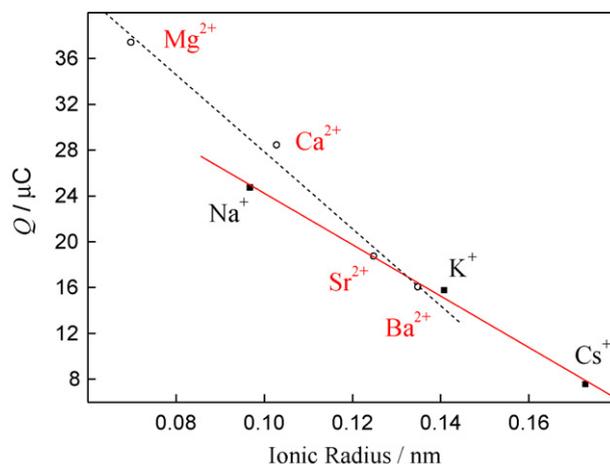
When amperometric measurements were recorded in solution for alkaline and earth-alkaline ions containing lithium ions, it was not observed a significant increase in the relative current. There is a small decrease in relative current for the lithium ions in the presence of magnesium, calcium and strontium. Thus, it can be assumed for those cations which are bigger than the charge density of the

**Table 1**

Relative current of the amperometric responses of the CPEM with spinel-type manganese oxide in TRIS buffer solution containing  $6.0 \times 10^{-4} \text{ mol L}^{-1}$  of alkaline and earth-alkaline metal ions in the absence and presence of lithium ions ( $6.0 \times 10^{-4} \text{ mol L}^{-1}$ ) under flow conditions.

Metallic cation	Relative current (%) <sup>a</sup>	
	Absence of lithium ions	Presence of lithium ions
Lithium	100	100
Sodium	33	105
Potassium	21	102
Cesium	10	101
Magnesium	50	90
Calcium	38	92
Strontium	25	94
Barium	8	95

<sup>a</sup> Relative current =  $\left(\frac{\text{Current signal of the cation}}{\text{Current signal of the lithium}}\right) \times 100\%$ .



**Fig. 7.** Curve obtained for peak charge at the electrode surface vs. ionic radius of alkaline (red solid line) and earth-alkaline ions (black dash line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

lithium ion, result in blocking of insertion tunnels on the surface of spinel.

#### 4. Conclusions

We have shown that CPEM with spinel manganese(IV) oxide under laminar flow regime provides good sensitivity measurement of lithium ion. The detection limit [34] was of  $1.73 \times 10^{-5} \text{ mol L}^{-1}$  lithium; this value was calculated from the signal to noise level of 3. The relative standard deviation (RSD) for 6 replicates of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  lithium was 1.7% and the analytical frequency was 96 determinations per hour. The peculiar behaviour observed for the modified electrode in flow injection measurements for high lithium ion concentrations provides significant information for calculation of apparent Gibbs energy of insertion and surface coverage of the electrode modified with spinel-type manganese oxide. The equilibrium constant of insertion/extraction of the lithium ions onto the spinel structure can also be calculated by Langmuir model. In the previous section, we demonstrated that insertion of lithium on the spinel structure over the electrode surface is a spontaneous process under the experimental conditions applied.

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