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Study of the potentiometric properties of spinel-type manganese oxide doped with gallium and anions $Ga_{0.02}Mn_{1.98}O_{3.98}X_{0.02}$ ($X = S^{2-}$ and F^{-}) as selective sensor for lithium ion

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ABSTRACT

This paper describes the development of a selective lithium ion sensor based on spinel-type manganese oxide doped with gallium and anions ($Ga_{0.02}Mn_{1.98}O_{3.98}X_{0.02}$, where $X = S^{2-}$ and F^{-}). Investigation was made of the influence of cationic and/or anionic doping agents on the potentiometric response of the sensor. Experimental parameters evaluated included the effect of the lithium concentration on activation of the sensor by cyclic voltammetry, the pH of the electrolyte solution, and the selectivity towards Li^{+} compared to other alkali and alkaline-earth metal ions. There was an important influence of the unit cell size of the material on the linear range, detection limit, and selectivity of the sensor. Reduction in the size of the tunnel for insertion of the lithium in the porous structure of the oxide directly affected the potentiometric performance of the electrode. Sensor performance increased in the order: $Ga_{0.02}Mn_{1.98}O_4 > Ga_{0.02}Mn_{1.98}O_{3.98}S_{0.02} > Ga_{0.02}Mn_{1.98}O_{3.98}F_{0.02}$. The observed super-Nernstian response could be explained by a mixed potential arising from two equilibria (redox and ion exchange) in the spinel-type manganese oxide. Sensitivity and the influence of pH on the electrode response were directly related to the doping agents present in the oxide structure.

1. Introduction

The attraction of spinel-type manganese oxide is due to the presence of tridimensional tunnels in the crystalline network. These enable topotactic reactions, with the insertion and extraction of lithium ions in the vacancies and interstitial spaces, which permits charge compensation by means of changes in the oxidation state of the manganese ion [1].

$$2Mn^{IV}O_{2(s)} + 2Li^{+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons Li_2[Mn_2{}^{(III)}O_4]_{(s)} + 2H^{+}{}_{(aq)} + \frac{1}{2}O_{2(g)} \qquad (1)$$

However, one of the main disadvantages related to the use of this material concerns the decrease in specific capacity during successive charge/discharge cycles, due to the Jahn-Teller effect [1]. This is an anisotropic distortion of the compact cubic symmetry formed by the O^{2-} ions in the spinel $LiMn_2O_4$, resulting in a tetragonal symmetry, and is one of the principal factors hindering use of the material in commercial applications [2,3]. In recent work, study of the partial substitution of manganese ions by other transition metal cations, as well as partial substitution of oxygen ions in manganese oxide by anions, revealed a decrease in the Jahn-Teller effect [4]. Attempts to improve the electrochemical performance of spinel-type manganese oxide have involved doping with divalent or trivalent metals (Ni, Co, Al, Ga, and Cr) to partially substitute the manganese ions in the spinel structure [5–8], or with anions to partially substitute the oxygens [9]. Simultaneous doping with cations and anions has also been investigated [5].

Doping with cations can improve the stability of the manganese oxide structure when the partial substitution is performed using a cation with smaller ionic radius than that of the manganese (0.65 Å) in the spinel structure. Amaral et al. [5] found that the ionic radius of cation dopants such as Al, Co, and Ga (ionic radii of 0.53, 0.60, and 0.63 Å, respectively) directly affected the unit cell parameter of manganese oxide, with values of 8.229, 8.230, and 8.231 Å, respectively, which were smaller than that of the pure spinel material (8.234 Å). In relation to the stability of the oxide, the partial substitution resulted in a decrease in the Mn^{3+}/Mn^{4+} ratio, due to substitution of the Mn^{3+} ions in the structure, which are responsible for the Jahn-Teller distortion [10]. In the case of doping with anions, the effect of the anion on the electrochemical

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performance of manganese oxide remains unclear. However, it is known that anionic doping reduces the dissolution of manganese in the electrolyte [5], consequently improving the structural stability of the oxide during insertion of the lithium ions [11,12].

Earlier work by our research group studied the effect of aluminum doping on the potentiometric performance of an electrode based on spinel-type manganese oxide for the selective detection of lithium ions [13]. It was found that the performance of the selective electrode was superior to that of non-doped manganese oxide [14], demonstrating that the Al(III) doping increased the structural stability of the material and improved the potentiometric response and sensitivity of the sensor. A super-Nernstian response of the sensor was obtained at pH 10. Similar improvement in electrochemical performance was found by Venugopal et al. [15], who studied the potentiometric response of a modified electrode consisting of spinel-type manganese oxide doped with Cr(III).

The present work describes a comparative study of the influence of anion doping (using S^{2-} and F^{-}) in gallium-substituted spinel manganese oxide on the potentiometric performance of an electrode selective to lithium ions. Evaluation was made of the effect of solution pH, as well as the selectivity towards lithium ions rather than other alkali metal and alkaline-earth metal ions. Investigation of the potentiometric behavior of the oxide provided insights into the sensor response mechanism.

2. Experimental

2.1. Reagents and solutions

All chemicals were analytical reagent grade and were used without further purification. The supporting electrolyte used for all experiments was a 0.1 mol L^{-1} Tris(hydroxymethyl) aminomethane (TRIS) buffer solution (pH = 10). A 0.010 mol L^{-1} lithium ions solution was prepared daily by dissolving LiCl (Merck) in 100 mL of TRIS buffer. For the study of interfering ions NaCl, KCl, RbCl, CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ were dissolved in the TRIS buffer.

2.2. Synthesis and characterization of the anion-doped gallium-substituted manganese oxide spinel

The anion-doped gallium-substituted manganese oxide was prepared and characterized by research group of the Prof. Bocchi [5]. The doped spinels were synthesized from by ε-MnO_2 [16], LiOH (Riedel de Haën), Ga_2O_3 (Aldrich) and Li_2S (Aldrich) or LiF (Aldrich) by solid-state reaction. When $Li_{1.05}Ga_{0.02}Mn_{1.98}O_4$ was the objective, the anionic salts were omitted. The precursors in the mole ratios $1.00(Mn_{1.98}+Ga_{0.02})(O_{1.98}+S_{0.02}):1.05Li$ and $1.00(Mn_{1.98}+Ga_{0.02})(O_{1.98}+F_{0.02}):1.05Li$ were prepared. After homogenization in a mortar, the precursor mixture was calcined in a tubular oven under static air at 750 °C for 72 h and then slowly cooled at a rate of −10 °C min^{-1}. A mixer mill (Spex Certiprep 8000 M) was used for milling the doped spinels for 30 min [5]. The anion-doped gallium-substituted manganese oxide was characterized by X-ray diffractometry (XRD) using an automated diffractometer (Shimadzu modelo XRD-6000) with Cu Kα radiation (30 kV and 40 mA) and graphite monochromator at a scan rate of 0.02° min^{-1} in an interval at 5° to 50°.

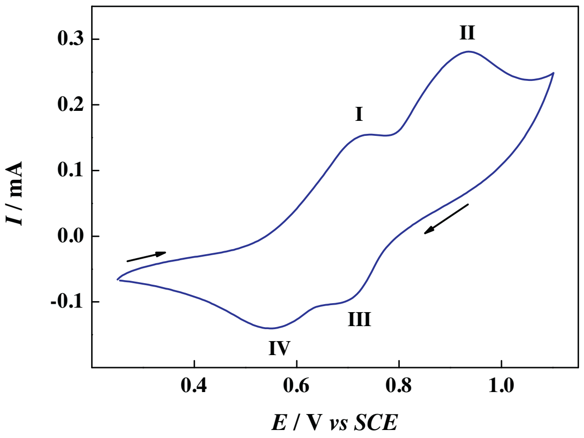

Fig. 1. Typical cyclic voltammogram obtained at 5 mV s^{-1} for CPEM with $Ga_{0,02}Mn_{1,98}O_4$ in 0.10 mol L^{-1} ions Li^+ in Tris buffer containing 0.1 mol L^{-1} in pH 10.

2.3. Preparation of the delithiated anion-doped gallium-substituted manganese oxide spinel

For conversion in delithiated form, the doped spinels $Li_{1.05}Ga_{0.02}Mn_{1.98}O_{3.98}X_{0.02}$ ($X = S^{2-}$ or F^{-}) was treated in an aqueous diluted sulfuric acid solution kept under constant stirring during 45 min. When the pH of this mixture became stable, the solution was decanted and the remaining solid material washed by decantation with deionized water, filtered and dried in air at 90 °C. Treatment of the spinel-type material with aqueous acid was found to result in conversion of the $Li_{1.05}Ga_{0.02}Mn_{1.98}O_{3.98}X_{0.02}$ to nearly pure $Ga_{0.02}Mn_{1.98}O_{3.98}X_{0.02}$, preserving the spinel structural. The manganese oxide has empty tetrahedral sites, and is designated as delithiated spinel and the Li^+ can re-enter in the empty sites of this oxide.

2.4. Selective Electrode Construction

The selective electrodes were prepared by carefully mixing 55% (m/m) of graphite powder (1-2 μm particle size, Aldrich), 25% (m/m) anion-doped gallium-substituted manganese oxide and 20% (m/m) of mineral oil (Aldrich). Those mixtures were prepared by magnetic stirring in Becker (50 mL) containing 20 mL of hexane. The final pastes were obtained by evaporation of the solvent. The modified carbon pastes were packed into an electrode body, consisting of a plastic cylindrical tube (o.d. 7 mm, i.d. 4 mm) equipped with stainless steel staff serving as an external electric contact. Packing paste was achieved by pressing the electrode surface (surface area of 12.6 mm^2) against a filter paper. Before the use, the electrodes were activated by cyclic voltammetry in 0.1 mol L^{-1} TRIS buffer solution (pH 10) containing lithium ions.

2.5. Apparatus

Cyclic voltammetric and potentiometric measurements were carried out with an μ-Autolab type III (Eco Chimie) controlled by a personal computer. All the measurements were performed at a constant temperature (25 °C), in a thermostated electrochemical cell. The cyclic voltammetric measurements were performed in a three-electrode cell using a carbon paste electrode modified (CPEM) with an anion-doped galium-substituted manganese oxide spinel as a working electrode (indicator electrode), saturated calomel electrode (SCE) as reference and platinum auxiliary electrode. The potential range was from 0.25 to 1.10 V (*vs.* SCE) at scan rate of 05 mV s^{-1}, and during the measurements the solution in the cell was not flowed. The potential differences between the working (CPEM) and reference electrodes were measured using the GPES software (Eco Chimie) by chronopotentiometry (zero current).

3. Results and discussion

3.1. Characterization of the $Ga_{02}Mn_{1.98}O_{3.98}X_{0.02}$

X-ray diffractograms of the delithied spinel $Ga_{0.02}Mn_{1.98}O_{3.98}X_{0.02}$ (Supplementary Material I) showed crystallographic