

Investigation of electrochemical lithium insertion in lamellar ternary oxides of the $M_xMnO_y \cdot zH_2O$ group

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Abstract

Synthesis of various X-birnessites ($X = Na, Al, Mg$) was performed from the oxidation of manganese hydroxide by an aqueous permanganate solution. Their structural and electrochemical characteristics are investigated. The influence of the exchanged cations and water content on the galvanostatic cycling curves has been studied. The best results are obtained for Mg-birnessite with a specific capacity of 130 Ah kg^{-1} recovered after 20 cycles at a $C/20$ discharge/charge rate for Mg birnessite. The cycling stability increased with increasing crystal lattice water content of the materials. © 1997 Published by Elsevier Science S.A.

Keywords. Layered structure; Manganese oxides; Lithium insertion

1. Introduction

While a great number of papers are devoted to three-dimensional MnO_2 oxides, specially for lithium-ion systems [1–5], little attention has been paid to layered structures. The interest of layered MnO_2 as the 3 V cathode material has been demonstrated a few years ago [6–9]. Lamellar MnO_2 are generally obtained by low-temperature synthesis involving a solution technique [7,8]. They constitute host lattices in which lithium ions can be easily inserted and withdrawn with fast kinetics and without major structural rearrangements. In particular, for the sol–gel birnessite [6] and disordered structures containing Bi ions [10], the high content of Mn^{4+} combined to the two-dimensional character of these crystal networks allow to reach attractive specific charges of around 200 Ah kg^{-1} .

In this work, we have taken advantage of the remarkable ionic exchange properties of Na-birnessite in order to synthesize various X-exchanged birnessites. We focus on the electrochemical properties of Al and Mg-birnessites which contain structural water. In particular, we give some details on the cycle life of these compounds using starved electrolytes in two-electrode cells.

2. Experimental

The mean oxidation state Z_{Mn} of manganese was determined by a chemical titration using ferrous sulfate with an

accuracy of ± 0.02 [11]. Chemical composition of the compounds was determined by elemental analysis.

X-ray diffraction (XRD) experiments were performed with a Inel diffractometer using $Cu K\alpha$ radiation.

The electrochemical measurements were performed in propylene carbonate, double-distilled, obtained from Fluka and used as received. Anhydrous lithium perchlorate was dried under vacuum at 200°C for 12 h. The electrolytes were prepared under a purified argon atmosphere.

The working electrode consisted of a stainless-steel grid with a geometric area of 0.5 cm^2 on which the lamellar manganese oxide (2 mg), mixed with graphite (20 wt.%), was pressed. Galvanostatic cycling experiments have been performed in a two-electrode cell. This cell was prepared inside the dry box by placing a clean metal lithium disk, a glass fiber separator soaked with the electrolyte solution, and the cathode pellet concerned into a Teflon container with two stainless-steel terminals.

3. Results and discussion

3.1. Synthesis and characterization of the lamellar ternary oxides

Synthesis of birnessites consists of oxidation of an Mn(II) salt in such a way as to obtain a material in which the manganese oxidation state is equal to 4 or is between 3 and 4 [12].

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Table 1
Chemical composition of the classical X-exchanged birnessites

	Chemical composition	% of Mn ⁴⁺	Z _{Mn}
Na-birnessite	Na _{0.28} MnO _{1.96} ·nH ₂ O	64	3.64
Mg-birnessite	Mg _{0.14} MnO _{1.96} ·nH ₂ O	64	3.64
Al-birnessite	Al _{0.093} MnO _{1.96} ·nH ₂ O	66	3.65

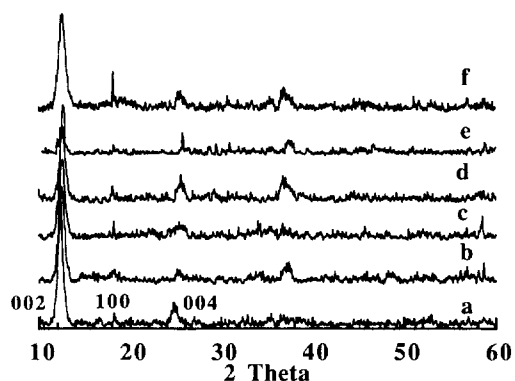


Fig. 1 XRD pattern (Cu K α) of (a) Mg-birnessite cathode; (b) Li_{0.1}Mg-birnessite; (c) Li_{0.2}Mg-birnessite; (d) Li_{0.3}Mg-birnessite; (e) Li_{0.5}Mg-birnessite; and (f) after the 1st charge.

Na-birnessite compound is well known to exhibit remarkable cationic exchange properties [13–15]. The quantitative exchange reaction of Na⁺ by Mⁿ⁺ ions is performed in an aqueous solution of magnesium or aluminum chloride under stirring at room temperature for one day. Then, the birnessite powder is recovered after filtration and dried in air at 80 °C for about 24 h.

The chemical composition of the compounds are summarized in Table 1.

The initial amount of Na⁺ ions (0.28 per Mn), weakly bonded to the lattice, is exchanged on the basis of a number of equal charges, i.e. 0.28 for M⁺ monovalent ions, 0.093 for M³⁺ trivalent ions. The mean oxidation state of manganese, Z_{Mn}, in the intercalated compound does not depend on the nature of the inserted cation. The three birnessites exhibit the

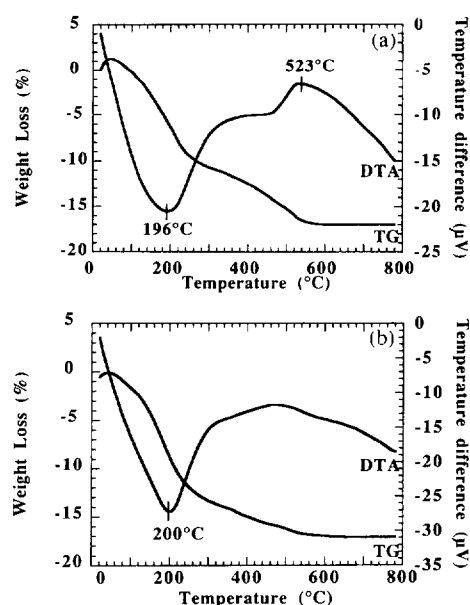


Fig. 2 Simultaneous thermal analysis (TGA and DTA) of (a) Mg-birnessite and (b) Al-birnessite.

same structure with very close unit cell parameters (Table 2). The hexagonal unit cell of the parent oxide (Na-birnessite) is maintained after the exchange procedure. Indeed, XRD patterns (Fig. 1(a)) clearly show a high preferred orientation with a strong peak around $d = 7.2$ Å, which accounts for the interlayer spacing in lamellar MnO₂ of the birnessite group [12–15].

The simultaneously recorded thermal analysis curves (GTA and DTA) of Mg-birnessite and Al-birnessite are shown in Fig. 2(a) and (b). The total weight loss up to 800 °C was around 17% for Mg-birnessite and Al-birnessite. A first and wide endothermic peak near 200 °C is observed for both compounds, corresponding to a weight loss of 12%, and is related to the departure of water molecules. This seems to indicate strongly bonded water since at 100 °C, only a low water content (< 2%) is given off.

Table 2
XRD data of birnessites (Bir)

Na-Bir (room temperature) Hexagonal	Mg-Bir (room temperature) Hexagonal	Mg-Bir (300 °C) Hexagonal	Al-Bir (room temperature) Hexagonal	Al-Bir (300 °C) Hexagonal
$a = 5.589$ Å $c = 14.398$ Å	$a = 5.610$ Å $c = 14.298$ Å	$a = 5.590$ Å $c = 14.298$ Å	$a = 5.600$ Å $c = 14.184$ Å	$a = 5.598$ Å $c = 14.184$ Å
7.199 Å (002)	7.149 Å (002)		7.092 Å (002)	
4.840 Å (100)	4.859 Å (100)	4.841 Å (100)	4.849 Å (100)	4.848 Å (100)
3.600 Å (004)	3.566 Å (004)		3.548 Å (004)	
2.424 Å (200)		2.422 Å (200) 1.962 Å (115) 1.794 Å (116)	2.422 Å (200)	2.422 Å (200)
1.823 Å (211)				1.776 Å (212)
1.567 Å (302)		1.615 Å (300) 1.569 Å (302)		1.572 Å (302)

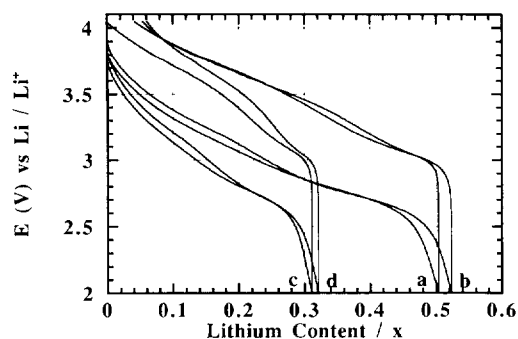


Fig. 3. Chronopotentiometric curves for the reduction/oxidation at $20 \mu\text{A cm}^{-2}$ of (a) Mg-birnessite, (b) Al-birnessite, (c) Mg-birnessite 300°C , and (d) Al-birnessite 300°C , in $1 \text{ M LiClO}_4/\text{PC}$ at 20°C .

Heating samples at 300°C for 5 h results in a disordered state of the initial hexagonal structure. The layered structure collapses when elimination of interlayer water occurs. The products obtained after heating Mg-birnessite at 700°C was the tetragonal phase, MgMn_2O_4 , and $\alpha\text{-Mn}_2\text{O}_3$ for Al-birnessite associated to a weight loss of around 4% clearly evidenced by GTA/DTA experiments.

3.2. Electrochemical behaviour of Mg-birnessite and Al-birnessite

Typical chronopotentiometric curves for the reduction/oxidation process ($20 \mu\text{A cm}^{-2}$) of Al-birnessite and Mg-birnessite in $1 \text{ M LiClO}_4/\text{PC}$ are shown in Fig. 3(a) and (b). These two compounds exhibit very similar curves, with a continuous decrease of the working potential, involving a faradaic yield of $\approx 0.5 \text{ Li}^+$ ions per mole of manganese.

XRD data performed on electrochemically reduced electrodes of Mg-birnessite, show that the hexagonal symmetry is maintained as lithium insertion proceeds (Fig. 1). The c parameter decreases as lithium insertion occurs in $\text{Li}_x\text{Mg}_{0.14}\text{MnO}_{1.96} \cdot n\text{H}_2\text{O}$ ($c = 14.298 \text{ \AA}$ for $x = 0$; $c = 13.600 \text{ \AA}$ for $x = 0.5$), but the order of magnitude for the c variation versus x is much lower than in the case of Li insertion in sol-gel birnessite (Fig. 4) [6]. Such a difference could be explained by the pillaring effect of the cationic species, Mg^{2+} or Al^{3+} , which limit the magnitude of the swelling process. The a parameter was calculated to be nearly the same, i.e., $a = 5.610\text{--}5.642 \text{ \AA}$. After a discharge/charge cycle has been carried out, the initial value of a and c parameter was practically restored (Fig. 3(f)) which confirms the stability of interlayer water in this lamellar compound.

In order to examine the role of structural water on electrochemical properties, we have investigated the electrochemical behaviour of heat-treated ($300^\circ\text{C}/5 \text{ h}$) Mg-birnessite and Al-birnessite (Fig. 3(c) and (d)). An important decrease of the faradaic yield was observed for these two heat-treated compounds since only $\approx 0.3 \text{ Li}^+$ ions can be inserted. Once again, in good accord with our previous results on sol-gel birnessite, we clearly outline the significant role of water in these layered structures.

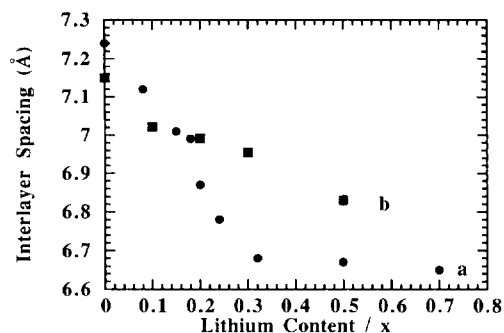


Fig. 4. Evolution of the interlayer spacing c for (a) sol-gel, and (b) Mg-birnessite.

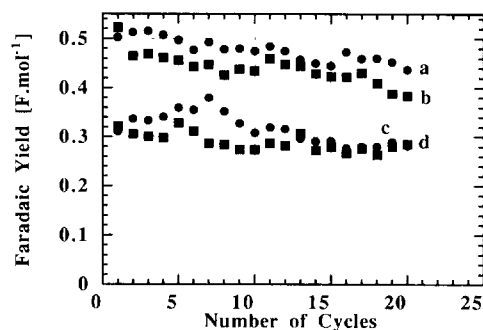


Fig. 5. Evolution of the specific capacity as a function of the cycles nos for (a) Mg-birnessite; (b) Al-birnessite; (c) Mg-birnessite 300°C , and (d) Al-birnessite 300°C , in $1 \text{ M LiClO}_4/\text{PC}$ at 20°C ($C/20$ discharge/charge rate).

Fig. 5 shows the evolution of the specific charge as a function of the number of cycles at a $C/20$ discharge/charge rate for Mg-birnessite and Al-birnessite and for the same samples treated at 300°C , for which interlayer water molecules have been removed. Hydrated compounds provided the best results. Al-birnessite shows a good cycling stability with a slight decrease of the capacity during the first cycles, and 75% of the initial capacity is recovered after the 20th cycle ($\approx 100 \text{ Ah kg}^{-1}$). For Mg-birnessite, a better cycling stability was observed. From an initial value of about 0.5 F/mol (130 Ah kg^{-1}), the specific capacity decreased slightly to about 0.46 F/mol after the 20th cycle (i.e. $>90\%$ of the initial value). The evolution of the capacity for the heat-treated Mg-birnessite and Al-birnessite exhibits an interesting behaviour, with a specific capacity of $\approx 80 \text{ Ah kg}^{-1}$ at the end of the 20th cycle. Comparison of these results with those obtained for the heat-treated form emphasizes the importance of the interlayer water which provides the 'elasticity' necessary for the host lattice to sustain a good reversibility of the lithium insertion reaction.

The cycling behaviour of closely related structures called Na and Li phyllosilicates has been investigated by Le Cras et al. [8]. Their results show a continuous drop of the specific capacity which does not exceed 150 Ah kg^{-1} after eighty cycles, but at a very low discharge/charge rate ($C/100$).

Our results in terms of rechargeable capacity and cycle life are then interesting as compared with data reported in

Ref. [7]. This work ascertains that water is stable as lithium insertion proceeds. Hence, these layered hydrated MnO_2 oxides can be considered with interest for practical use in rechargeable 3 V lithium batteries.

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