

Synthesis and Characterization of Lamellar MnO₂ Obtained from Thermal Decomposition of NaMnO₄ for Rechargeable Lithium Cells

S. Bach,^{*1} J. P. Pereira-Ramos,^{*} and N. Baffier[†]

^{*}CNRS UM 28, Electrochimie, Catalyse et Synthèse Organique, 2 rue H. Dunant, 94320 Thiais, France; and [†]ENSCP, CNRS URA 1466, Chimie Appliquée de l'Etat Solide, 11 rue P. et M. Curie, 75231 Paris, Cedex, France

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Thermal treatment (600–800°C) in air of solid NaMnO₄ induces the reduction of Mn(VII), leading to the formation of ternary oxides: α-Na_{0.7}MnO₂ around 500°C and α-NaMnO₂ for higher temperatures (800°C). Sulfuric acid treatment of these compounds leads to the formation of a lamellar phase with a highly preferred orientation: MnO_{1.86} · nH₂O (0.6 ≤ n ≤ 0.7). The lithium insertion process in this compound has been studied in 1 M LiClO₄ solution in propylene carbonate. A high depth of discharge is then achieved, ≈0.82 F/mole. Cycling experiments carried out in the potential window 4.2–3 V showed that after the 5th cycle, about 0.62 F · mole⁻¹ (180 Ah · kg⁻¹), i.e., 84% of the initial capacity, is recovered. © 1995 Academic Press, Inc.

1. INTRODUCTION

Layered MnO₂ host lattices have proven to be of great interest as rechargeable cathodic material for lithium batteries. In previous works (1, 2), we have clearly shown the interest of using the sol-gel technique to prepare high-performance and new-layered MnO₂. The cathodic material called "sol-gel birnessite" with the formula MnO_{1.86} · nH₂O (0.6 ≤ n ≤ 0.7) has an open structure in which lithium intercalation occurs over an unusually wide lithium concentration range (Δx ≈ 0.8) at a working potential of ca. 2.9 V which makes this material very attractive. Recent studies proved that interlayer water was stable during the insertion-deinsertion process (3).

The versatility of the MnO₂ system offers numerous synthetic ways to optimize its electrochemical behavior in secondary lithium batteries.

The purpose of this paper is to investigate a synthesis, by a new and simple solid route, of a lamellar manganese oxide MnO₂ prepared from the thermal decomposition of sodium permanganate. Preliminary structural and electrochemical properties related to this compound are described and discussed.

¹ To whom correspondence should be addressed.

2. EXPERIMENTAL

Sodium permanganate NaMnO₄ obtained from Fluka was used in the present work.

The mean oxidation state Z_{Mn} of manganese was determined by a chemical titration using ferrous sulfate with an accuracy of ±0.02 (4).

X-ray diffraction experiments were performed with an Inel diffractometer using the CuKα radiation. Thermal analysis measurements were performed in air at heating rates of 10°C · min⁻¹ using a Netzsch STA 409 analyzer with recording of weight losses (GTA).

The electrochemical measurements were performed in propylene carbonate, twice distilled, obtained from Fluka and used as received. Anhydrous perchlorate was dried under vacuum at 200°C for 12 hr. The electrolytes were prepared under a purified argon atmosphere. The working electrode consisted of either a stainless steel or a gold grid with a geometric area of 1 cm² on which the lamellar manganese oxide (2 mg), mixed with graphite (20% by weight), was pressed. The cell has already been described (5); it contains electrolyte and lithium in excess. Both sides of the electrode were dipped in a flooded electrolyte.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

The thermogravimetric curve of solid NaMnO₄ is shown in Fig. 1. A total weight loss of 28% was observed. From 100 to 400°C, the sample loses appreciable mass (24.92%) which probably corresponds to the departure of oxygen. A last weight loss of 3% was observed at 650°C.

X-ray diffraction patterns performed on NaMnO₄ treated at different temperatures are shown in Fig. 2. The starting material corresponds to the sodium permanganate (Fig. 2a). From 400°C (Fig. 2b), one well-defined diffraction line with *d*-spacing, 5.55 Å (002), and two badly defined diffraction lines, 2.78 Å (004) and 2.02 Å (0.13), character-

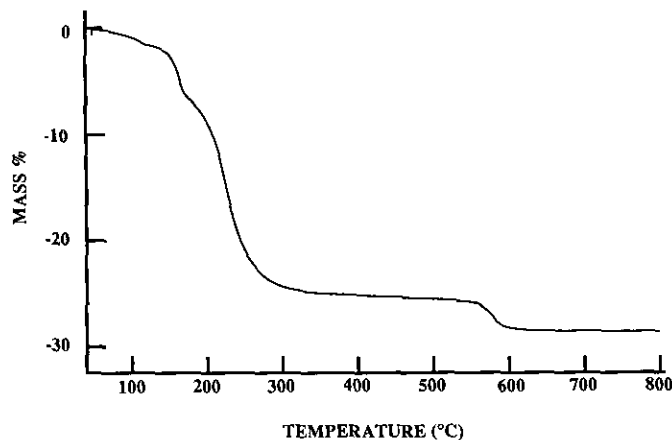
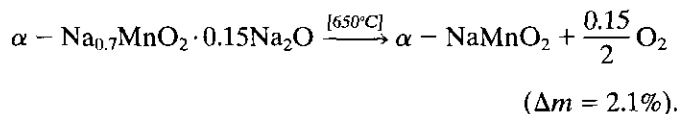
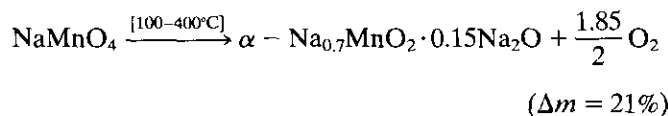


FIG. 1. Thermal analysis (GTA) of NaMnO₄ obtained from Fluka.

istic of the hexagonal ternary oxide α -Na_{0.7}MnO₂ appear. Thus, at this temperature, only 70% of the sodium ions have reacted with the manganese, and the remaining Na⁺ ions (30%) are present in the form of Na₂O adsorbed at the surface of the compound. The structure of α -Na_{0.7}MnO₂ consists of layers of edge-sharing MnO₆ octahedra with Na atoms located between these layers. The perpendicular distance between two consecutive layers is 5.5 Å. Moreover, it is apparent that this compound exhibits an important preferred orientation. Finally, at 700°C (Fig. 2c), after the last weight loss observed in TGA, the precedent diffraction lines have disappeared and the diagram characteristic of α -NaMnO₂ was observed, corresponding to the reaction of all sodium ions.

From these results, the successive weight loss on GTA can be explained by the following equations:



It appears that the thermal treatment (600–800°C) in air of solid NaMnO₄ induces the thermal reduction of Mn(VII), leading to the formation of ternary oxides: α -Na_{0.7}MnO₂ around 500°C and α -NaMnO₂ for higher temperatures (800°C).

Sulfuric acid treatment of these ternary oxides (α -Na_{0.7}MnO₂ and α -NaMnO₂) allows the sodium ions to be released into the solution and provokes disproportionation of Mn³⁺ ions into soluble Mn²⁺ ions and insoluble Mn⁴⁺

ions. Thus, the solid network progressively transforms into MnO₂. The material obtained was then filtered, rinsed with water, and dried at 60°C for 17 hr.

As confirmed by X-ray diffraction of the product (Fig. 3a) and the measured oxidation state of manganese $Z = 3.69$, the acid treatment leads to the formation of a lamellar

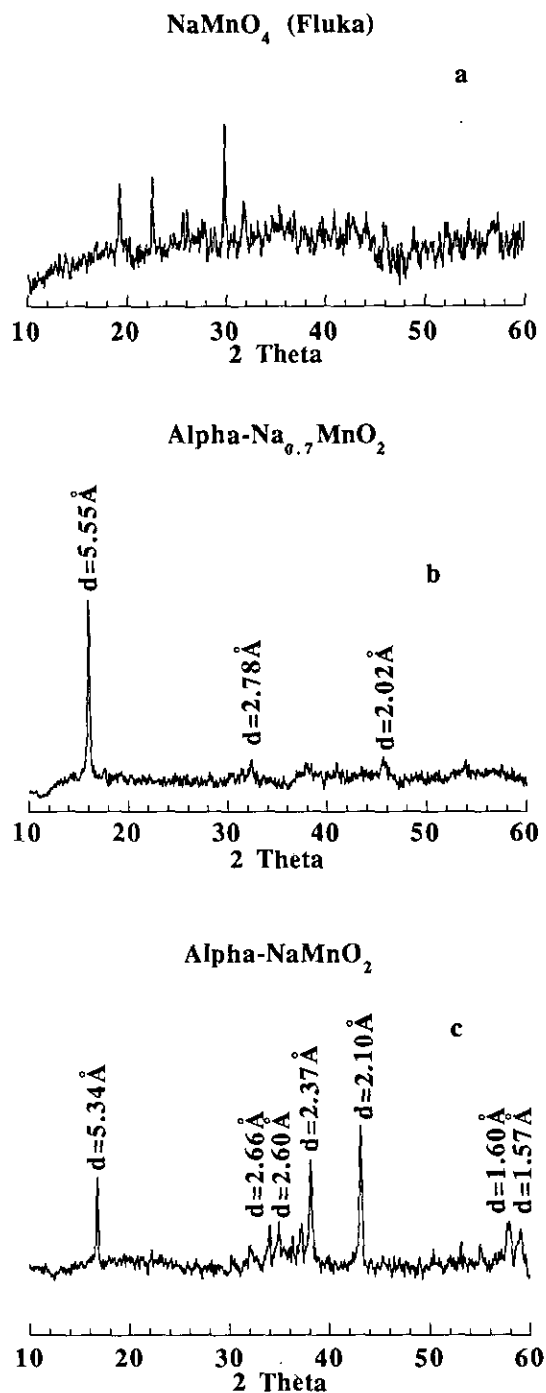


FIG. 2. Evolution of the X-ray diffraction patterns (CuK α) of NaMnO₄ at RT (a) and heated at 400°C/5 hr (b) and 700°C/5 hr (c).

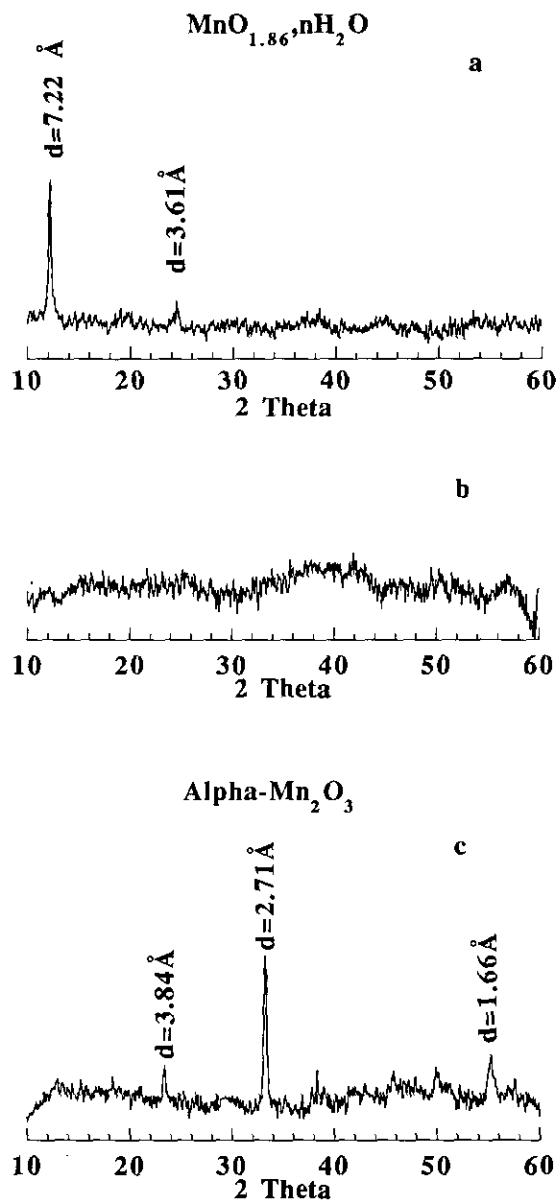


FIG. 3. Evolution of the X-ray diffraction patterns ($\text{CuK}\alpha$) of the lamellar manganese oxide at RT (a) and heated at $300^\circ\text{C}/2$ hr (b) and $600^\circ\text{C}/2$ hr (c).

phase: $\text{MnO}_{1.86} \cdot n\text{H}_2\text{O}$ ($0.6 \leq n \leq 0.7$). Indeed, one well-defined peak appears centered at 7.22 \AA , and another badly defined one appears at 3.61 \AA ; only 001 and 002 peaks appear, which indicate stacking of the layers parallel to the (a, b) plane over large domains. As in the case of the sol-gel synthesis, this new way of synthesis allows this lamellar manganese oxide with a highly preferred orientation to be obtained.

When $\text{MnO}_{1.86} \cdot n\text{H}_2\text{O}$ was heat-treated at 300°C (Fig. 3b), after the departure of water molecules, the X-ray diffraction pattern shows an important amorphous charac-

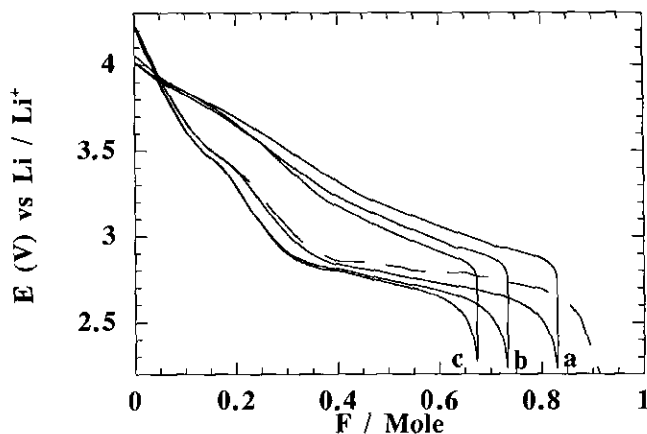


FIG. 4. Influence of the current density on $\text{MnO}_{1.86} \cdot n\text{H}_2\text{O}$ electrode in $1 \text{ M LiClO}_4/\text{PC}$ at RT. (a) $C/80$; (b) $C/20$; (c) $C/8$. The sol-gel lamellar compound for comparison is represented with dotted lines ($C/80$).

ter, while a heat treatment performed at 600°C leads to the formation of bixbyite $\alpha\text{-Mn}_2\text{O}_3$ (Fig. 3c).

3.2. Electrochemical Results

Typical chronopotentiometric curves for the reduction-oxidation process of the lamellar compound in 1 M LiClO_4 solution in propylene carbonate is shown Fig. 4. This curve is very similar to the sol-gel birnessite with the same insertion steps: the first step consists of a substantial decrease in the working potential from 4.2 to 2.85 V corresponding, as shown by previous X-ray experiments (6), to a hexagonal to monoclinic distortion originating from a gliding of MnO_6 layers, one with regard to the other, and a second step which appears as a gradual decrease in cell voltage below 2.85 V due to the Li accommodation in this new monoclinic phase (6). A high level of discharge is then achieved,

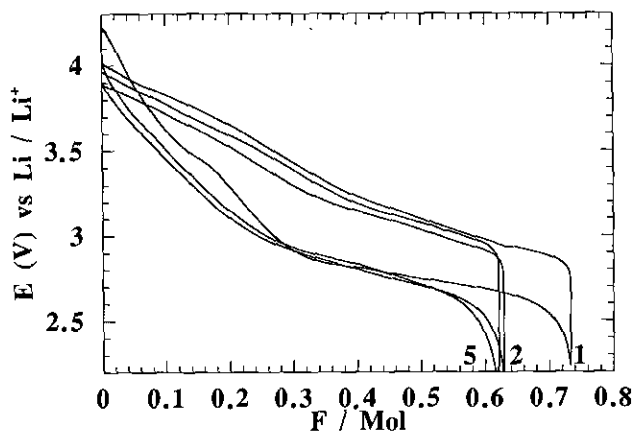


FIG. 5. Evolution of cycling properties of $\text{MnO}_{1.86} \cdot n\text{H}_2\text{O}$ in $1 \text{ M LiClO}_4/\text{PC}$ at RT ($C/20$). The number of the cycle is indicated on the figure.

≈0.82F/mole, which is very close to that exhibited by the sol-gel compound MnO_{1.85}·0.7H₂O (0.9 F·mole⁻¹).

A weak loss of its specific capacity with the discharge rate is observed. Moreover, the decrease in the total faradaic yield is especially ascribed to the second step, whereas the first process, requiring the insertion of about 0.35 F·mole⁻¹ per mole of compound, is never significantly affected.

Reversibility of the lithium insertion process has been evaluated from cycling experiments carried out in the potential range 4.2–3 V (Fig. 5). The discharge curves reported as a function of the number of cycles for the lamellar compound at 40 μA·cm⁻² (C/20) in 1 M LiClO₄/PC at room temperature reveals again that this kind of lamellar compound is highly rechargeable. Indeed, after the 5th cycle, about 0.62 F·mole⁻¹ (180 Ah·kg⁻¹), i.e., 84% of the initial capacity, is recovered.

We have demonstrated that high-performance lamellar MnO₂ could be prepared using an original and easy method of synthesis.

However, these preliminary results remain slightly infe-

rior to those obtained in the case of sol-gel birnessite (1) and have to be extended to other permanganate salts (AMnO₄; A = K, Li, Ba, ...).

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REFERENCES

1. S. Bach, J. P. Pereira-Ramos, N. Baffier, and R. Messina, *Electrochim. Acta* **36**, 1595 (1991).
2. P. Le Goff, S. Bach, J. P. Pereira-Ramos, N. Baffier, and R. Messina, *Solid State Ionics* **61**, 309 (1993).
3. P. Le Goff, S. Bach, J. P. Pereira-Ramos, and N. Baffier, *J. Mater. Chem.* **4**, 133 (1994).
4. M. J. Katz, R. C. Clarke, and W. F. Nye, *Anal. Chem.* **28**, 507 (1956).
5. J. P. Gabano, M. Broussely, J. P. Pereira-Ramos, R. Messina, and J. Perichon, French Patent No. 8501309, 1985.
6. P. Le Goff, S. Bach, J. P. Pereira-Ramos, and N. Baffier, *J. Mater. Chem.* **4**, 875 (1994).