



Synthesis and characterization of LiMn_2O_4 for use in Li-ion batteries

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Abstract

Lithiated spinel manganese dioxide was synthesised from electrochemical MnO_2 and Li_2CO_3 with deficiency or excess lithium ($\text{Li}_x\text{Mn}_2\text{O}_4$, $0.8 < x < 1.3$) for use in $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ and Li-ion cells. Micron-sized $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ prepared at 730°C showed high Li utilization, excellent cyclability and good rate capability with an initial discharge capacity of 123 mA h/g and 10% discharge capacity reduction after 20 cycles. Different types of commercial carbonaceous materials were also investigated with respect to their electrochemical performance vs. Li. Unoptimised Li-ion cells, using $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ prepared at 730°C as the cathode material, EC-DMC-LiPF₆ electrolyte and carbon fibres, showed promising performance characteristics. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since the introduction by Sony of its rechargeable lithium-ion battery in 1990 [1], much research effort has been directed to the development of lithium-ion systems by several research laboratories such as Bellcore and battery manufacturers worldwide in order to meet the demands of reliable, safe, high-energy density and environmentally friendly portable power sources. It seems that in the late 1990s lithium-ion batteries have become the state of the art in portable consumer electronics and are prime candidates for use in powering electric vehicles [2–4]. This is quite understandable since lithium-ion cells, with cathode material one of the high-voltage oxides LiNiO_2 , LiCoO_2 , LiMn_2O_4 and anode material some form of carbon, have a specific capacity comparable to that of Ni–Cd rechargeable batteries, with an energy density almost 3 times as high. Of the three above-mentioned transition metal oxides, LiMn_2O_4 shows exceptional promise due to its low cost, low toxicity and excellent voltage profile characteristics. On the other hand, many types of carbon (graphite natural or synthetic, petroleum coke, mesocarbon, carbon black, etc.) have been proposed and used for anode materials with their performance being greatly de-

pendent on their compatibility with the electrolyte system [5]. Although currently available Li-ion systems use some form of disordered carbon, it seems that the future trend is the use of graphite or graphitised carbon, which delivers specific capacities close to the theoretical value of 370 mA h/g [6]. The disadvantage of the highly ordered graphites is that they are more sensitive to the electrolyte solution than the disordered carbons [5]. In addition, different forms of disordered carbon such as carbon fibres or mesocarbon microbeads are also considered mainly due to the good cyclability that they exhibit [2,7,8].

In this work, which is part of a project in collaboration with Germanos Batteries S.A., we present an overview of our attempt to develop a Li-ion system with $\text{Li}_x\text{Mn}_2\text{O}_4$ as the cathode material. To this extent, we report on the optimization of synthesised spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ with respect to its lithium utilization, cyclability and rate capability by controlling the synthesis conditions and particle size of the prepared material and by correlating its structural, physical and transport properties with its electrochemical performance. In addition, we present the evaluation of the electrochemical performance of different commercial carbonaceous materials as evidenced by their cycling characteristics and comment on their compatibility with several organic solvent electrolyte systems. Finally, we show preliminary results of unoptimised Li-ion systems under in-

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vestigation, employing graphite and carbon fibre anode electrodes.

2. Experimental

Lithiated spinel manganese dioxide ($\text{Li}_x\text{Mn}_2\text{O}_4$, $0.8 \leq x \leq 1.3$) was prepared by solid-state reaction of commercially available electrochemical MnO_2 (EMD) (Tosoh Hellas), widely used for Zn– MnO_2 batteries, with Li_2CO_3 (Aldrich) at temperatures ranging from 450 to 850°C. Having determined the actual manganese content of the EMD to be $58.8\% \pm 0.5\%$ w/w by energy dispersive spectroscopy (EDS), the appropriate amount of Li_2CO_3 was determined in order to obtain the required excess or deficiency of lithium in $\text{Li}_x\text{Mn}_2\text{O}_4$. The Li content of some of the final products was determined by atomic absorption spectroscopy (AAS) and was within 2–5% of the nominal values.

The electrolytes used were LiPF_6 1 M with ethylene carbonate (EC)-dimethyl carbonate (DMC) (2:1 v/v), LiPF_6 1 M with propylene carbonate (PC)-EC-DMC (1:1:2 v/v) and LiClO_4 1 M with EC-diethoxy ethane (DEE) (1:1 v/v). LiPF_6 (Aldrich, 99.99 + %) and LiClO_4 (Fluka, > 99%) was used as received. PC (Aldrich, 99%), EC (Fluka, > 99%), DEE (Aldrich, 98%) and DMC (Fluka, > 99%) were dried with molecular sieves 4 Å. PC was also distilled under reduced pressure and the middle fraction was collected. All mixtures were made in a glove box, under argon atmosphere, where moisture content was less than 2 ppm.

Five different commercial carbonaceous materials were investigated: (a) Synthetic graphite 1–2 μm (Aldrich), (b) synthetic graphite < 325 mesh (Johnson Matthey), (c) mesocarbon microbeads MCMB-6-28S (Osaka Gas), (d) carbon fibre AGM-98 and synthetic graphite A-625 < 200 mesh (Asbury Mills).

Cathode electrodes were formed by pressing a mixture of the active material with acetylene black and EPDM binder with a 89:10:1 ratio onto aluminium disk current collectors. Anode electrodes were made by mixing the carbon powders with acetylene black and PVDF binder at a 90:5:5 ratio in cyclopentanone. The resulting slurry was deposited onto a copper disk, and the electrodes were pressed. Electrochemical measurements were conducted galvanostatically using an Arbin battery test system and two electrode cells. Cells were assembled in an argon filled glove box.

3. Results and discussion

3.1. Optimised lithiated MnO_2 as cathode material

The X-ray diffraction patterns of LiMn_2O_4 prepared at temperatures below 730°C exhibit extra peaks correspond-

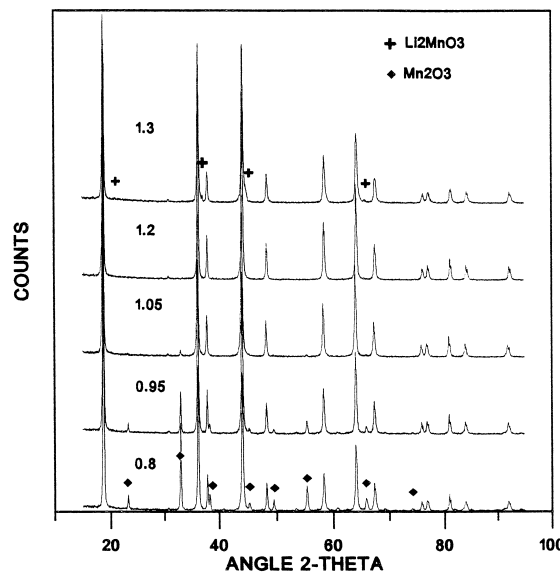


Fig. 1. XRD patterns of $\text{Li}_x\text{Mn}_2\text{O}_4$ with various initial Li stoichiometry ($0.8 < x < 1.3$) prepared at 700°C. The peaks corresponding to the Mn_2O_3 and the Li_2MnO_3 phases are marked with ◆ and +, respectively.

ing to a Mn_2O_3 phase present, the proportion of which decreases with increasing firing temperature. The lattice parameter of the sample prepared at 730°C obtained after fitting was 8.232 Å, which is in agreement with that reported in the literature for cubic LiMn_2O_4 [9]. Fig. 1 shows the X-ray diffraction patterns of samples prepared with deficiency or excess lithium ($0.8 \leq x \leq 1.3$) at a firing temperature of 700°C. It can be seen that within the range $1.1 < x < 1.25$, the as-prepared material is single-phase spinel $\text{Li}_x\text{Mn}_2\text{O}_4$. At other stoichiometries, phases of Mn_2O_3 and Li_2MnO_3 appear as impurities for $x < 1.1$ and $x > 1.25$ respectively, as identified by the corresponding peaks in the XRD patterns of Fig. 1. The Li_2MnO_3 phase, the formation of which has been proposed to be due to a disproportionation reaction of $\text{Li}_x\text{Mn}_2\text{O}_4$ [10], is usually identified by either of the two XRD peaks at $2\theta \sim 37^\circ$ or $\sim 45^\circ$ which are of comparable intensity [10,11]. In Fig. 1, it is seen that the former can clearly be identified as a peak whereas the latter is observed as a sideband of the LiMn_2O_4 (004) peak. This peak broadening is probably a consequence of the small particle size and poorer crystallinity as compared to other work [12,10] in which the synthesis temperature ranged from 750–900°C. The preparation of single phase lithiated manganese dioxide with excess Li up to $x = 1.15$ and $x = 1.20$ has been reported previously by Tarascon et al. [12] and Gao and Dahn [10], respectively. In the second of these reports, it is determined that the amount of excess Li incorporated into the cubic spinel phase is synthesis temperature and cooling rate-dependent. In particular, lower synthesis temperature and/or cooling rates favour the preparation of single-phase $\text{Li}_x\text{Mn}_2\text{O}_4$.

FTIR spectroscopy was used in different aspects of the characterization of the as-prepared materials such as the

determination of the completion of the solid-state reaction, structural identification of the stoichiometric material (LiMn_2O_4) that exhibits 4 bands in the mid- and far infrared spectral regions (620, 500, 350, 250 cm^{-1}) and information on the electrical conductivity from the plasma edge [13]. The dc and ac conductivity of MnO_2 [14] is 1–2 orders of magnitude higher than that of the spinel LiMn_2O_4 material, suggestive of hopping conduction via the small polaron in the former [15,16].

Galvanostatic measurements for the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells were performed between the limits 3.5–4.3 and 3.5–4.7 V with a charge/discharge rate of C/8. The results presented were obtained for at least four different cells for any of the experiments referred to. The voltage profiles obtained with the 4.7 and 4.3 V upper limits were very similar demonstrating the good oxidative stability of the electrolyte. Fig. 2 shows the first cycle voltage profiles corresponding to cells charged to 4.7 V with cathodes of LiMn_2O_4 and $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$, prepared at 730°C, with first discharge capacities of 120 mA h/g and 127 mA h/g respectively corresponding to 0.82 and 0.87 mol of Li per mol of active cathode material. These values are reduced to 115 mA h/g and 123 mA h/g when the cells are cycled between 3.5 and 4.3 V. Furthermore, Fig. 3 shows the cyclability of these two cathode materials. It can be seen that the discharge capacity of the stoichiometric material decreases by about 13% after 20 cycles while that of the $x = 1.05$ material, by about 10%. This is in agreement with previous results showing that addition of excess Li to stoichiometric LiMn_2O_4 increases the materials' cyclability [12,17,18].

Spinel $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ was ground in a vibrating ball mill in order to reduce the particle size and its distribution. Material ground for 9 h showed a tenfold increase in specific surface area with a narrow particle size distribu-

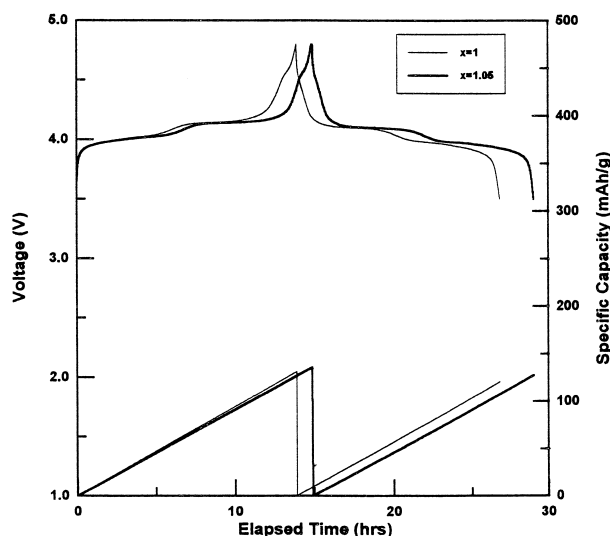


Fig. 2. Typical first cycles between 3.5 and 4.7 V for the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells obtained with different Li stoichiometries ($x = 1.0$ and 1.05).

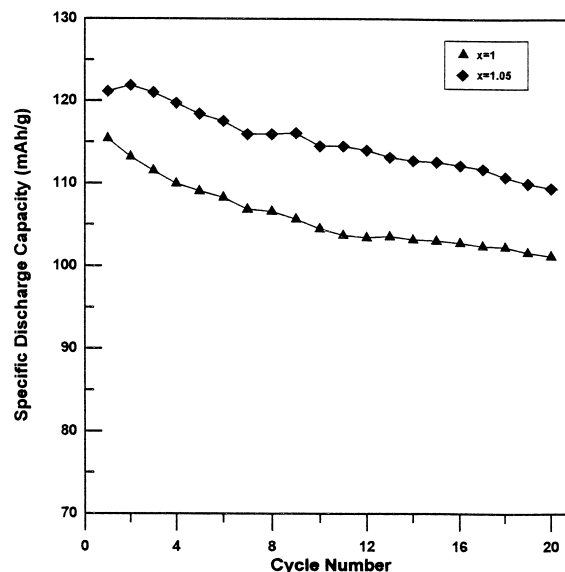


Fig. 3. Specific discharge capacity vs. cycle number for $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells cycled between 3.5 and 4.3 V at a C/8 rate.

tion [13]. The increase of the discharge current rate from C/8 to 1C decreases the discharge capacity of as-prepared LiMn_2O_4 by about 10% (0.78 to 0.70). The same rate increase on the $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ ground material reduces its discharge capacity by about 5% (0.83 to 0.79). Thus, material prepared with 0.05 Li excess at 730°C with uniform, micron-sized particles shows high Li utilization, excellent cyclability and good rate capability.

3.2. Different carbons as anode materials

Three types of synthetic graphite, mesocarbon microbeads and carbon fibre, all commercially available, were investigated. As confirmed by XRD measurements, the mesocarbon microbead sample was highly graphitised, whereas the carbon fibre was disordered. Electrochemical measurements were performed in galvanostatic mode at a current density of 100 $\mu\text{A}/\text{cm}^2$ both for charge and discharge. The specific capacity corresponding to the first discharge and the charge:discharge ratio of subsequent cycles of the five different carbon samples examined, is summarised in Table 1. The low ratios of the first charge-to-discharge cycle is related to the initial formation of the 'solid-electrolyte interface' (SEI), as discussed later. In subsequent cycling, the cycling efficiency is significantly enhanced, and as the number of cycles is increased, the efficiency increases approaching unity. At the 20th cycle, the charge:discharge ratio is between 0.95 and 0.98 for all types of carbon.

In Fig. 4, we present the voltage profile corresponding to the initial discharge/charge behaviour of GAL graphite. Initially, the cell voltage drops sharply from the OCV at assembly to about 1.4 V. At this voltage, a small plateau

Table 1

Specific capacity corresponding to the first discharge and charge:discharge ratios for subsequent cycles of the five different samples of commercial carbon investigated

Company	Type	Code	Electrolyte	First specific discharge capacity (mA h/g)	Cycling efficiency				
					1st	2nd	5th	10th	20th
Aldrich	Synthetic Graphite	(GAL)	EC-DMC + LiPF ₆	398	0.82	0.90	0.95	0.94	0.98
Asbury	Carbon fibres	(CF)	EC-DMC + LiPF ₆	327	0.59	0.90	0.96	0.98	0.97
Asbury	Synthetic Graphite	(GAS)	EC-DMC + LiPF ₆	349	0.56	0.84	0.92	0.97	0.97
Osaka	Mesocarbon Microbeads	(MCMB)	EC-DMC + LiPF ₆	330	0.79	0.80	0.97	0.98	0.98
Osaka	Mesocarbon Microbeads	(MCMB)	PC-EC-DMC + LiPF ₆	311	0.85	0.87	0.85	0.89	0.95
Johnson Matthey	Carbon Graphite	(GJM)	EC-DMC + LiPF ₆	380	0.83	0.96	0.82	0.91	0.96

appears, followed by a second one much more pronounced at a voltage of about 0.8 V. These two plateaus are manifested by peaks in the incremental capacity, calculated for the first lithiation (inset of Fig. 4), and are attributed to the formation of the 'SEI'. It is an established fact [6] that the reduction of EC occurs at 0.8 V, suggesting that the latter peak is due to this reaction. By the fact that the former peak has approximately 30 times less capacity than this, it can be assumed that it is due to a secondary passivating reaction most probably to the reduction of the DMC component of the electrolyte system [19]. Both these peaks do not appear in the subsequent charge/discharge cycles and correspond to the irreversible capacity of the first lithiation. The lower voltage region (0.3–0.02 V) corresponds to the intercalation of carbon and is also

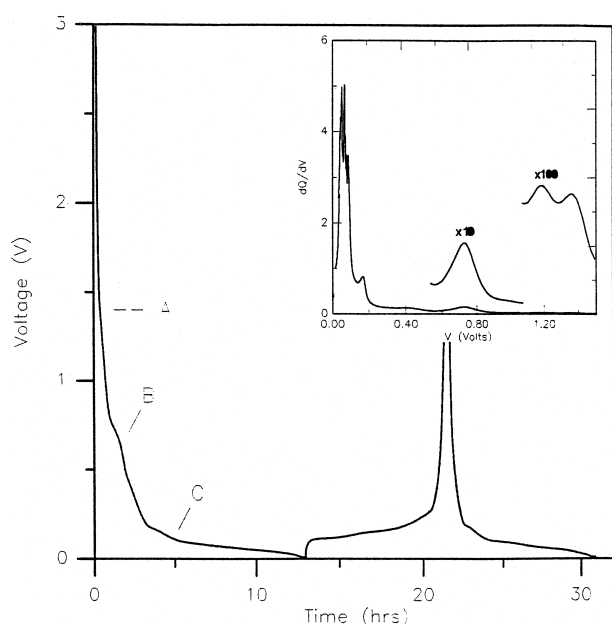


Fig. 4. The first lithiation followed by the first charge/discharge of synthetic graphite (GAL). In the inset is shown the incremental capacity for the first lithiation.

manifested by a series of peaks in the incremental capacity curve. These peaks are attributed to staging phenomena in the graphitic structure [20] and appear similar both at the first lithiation as well as at the subsequent charge/discharge cycles, but their position shows a dependence on the type of graphitic material.

3.3. Li-ion cells

Two of the carbonaceous materials investigated, namely the carbon fibres (CF) and synthetic graphite (GAL), were used in laboratory Li-ion cells incorporating the optimised cathode material and EC-DMC-LiPF₆ as electrolyte. Carbon fibres were chosen, since recently it has been pointed out that microfibrils as anode materials are expected to increase Li-ion cell efficiency [2].

These preliminary results based on our C/Li_xMn₂O₄ system are presented in Fig. 5a,b. The positive and negative electrode masses of these cells were estimated by taking the values that give equal capacities for the first discharge of Li_xC₆ vs. Li to 20 mV and the first charge of Li_{1.05}Mn₂O₄ vs. Li to 4.3 V giving mass ratios of 3.3 and 2.7 for graphite and carbon fibres, respectively. The current density used was 0.1 mA/cm² and the cells were cycled between 2.3 and 4.3 V exhibiting an average voltage of 3.9 V. The comparison of the performance of the two unoptimised cells clearly shows improved characteristics of the carbon fibre containing cell relative to that having a graphite anode. The latter exhibits specific capacity values significantly lower than expected [21] with very poor stability manifested by a 40% capacity decrease after 20 cycles. Furthermore, the capacity shows a continuously decreasing trend with cycling. Contrary to this, the former cells show a much lower capacity fading after 20 cycles (~20%), with approximately half of this reduction occurring between the first two cycles. The reversible specific capacity shows a tendency to stabilise at about 50 mA h/g after 25 cycles which is about the same as the capacity of

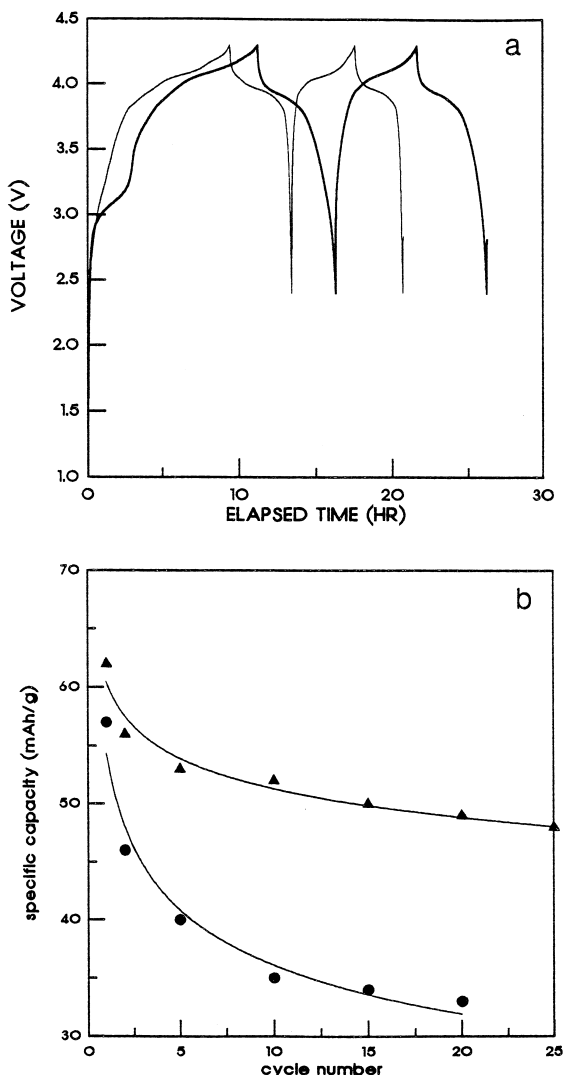


Fig. 5. (a) Voltage profiles of unoptimised $C/Li_xMn_2O_4$ cells. Thick solid line: carbon fibre anode, thin line: synthetic graphite anode. (b) Specific discharge capacity vs. number of cycles of the Li-ion cells shown in (a). Triangles: carbon fibre anode, circles: synthetic graphite anode.

balanced $LiMn_2O_4$ /petroleum coke cells with a comparable electrolyte appearing in the literature [22].

4. Conclusions

The characterization of spinel $Li_xMn_2O_4$ cathode material, prepared at different synthesis temperatures, cooling rates and excess lithium as well as post-calcination grinding, resulted in the optimization of the cathode material for use in Li-ion battery applications. Thus, material prepared with 0.05 Li excess at $730^\circ C$ with uniform, micron-sized particles shows high Li utilization, excellent cyclability

and good rate capability. Different carbonaceous materials used show a good cycling efficiency as a result of compatibility with the electrolyte systems used. Further work is underway in order to optimise these carbon materials with respect to their reversible capacity. Preliminary results of unoptimised, with respect to electrode mass balance, $C/Li_xMn_2O_4$ Li-ion cells show that carbon fibres are promising anode materials.

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