

Synthesis and characterization of $\text{Li}_2\text{M}_x\text{Mn}_{4-x}\text{O}_8$ ($\text{M} = \text{Co}, \text{Fe}$) as positive active materials for lithium-ion cells

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Abstract

We describe the preparation and the electrochemical properties of $\text{Li}_2\text{M}_x\text{Mn}_{4-x}\text{O}_8$, spinel-structured compounds. The results demonstrate that these materials may operate as high-voltage cathodes in new concept lithium-ion batteries. An example of these batteries has been fabricated and successfully tested. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Spinel; Lithium intercalation; Lithium-ion battery

1. Introduction

One of the recent trends in the lithium-ion battery technology is focused on the characterization and development of high-voltage cathodes. Few classes of compounds, operating in the near 5 V range have been reported. Some relevant example are: $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ [1]; LiNiVO_4 [2]; $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$ [3] and $\text{Li}_2\text{Co}_{1+x}\text{Mn}_{3-x}\text{O}_8$ [4]. We have also been involved in this line of research, initially with attention to the $\text{LiCo}_y\text{Ni}_{1-y}\text{VO}_4$ spinel family [5] and more recently, to high-voltage compounds of general formula $\text{Li}_2(\text{M}_1\text{M}_2)_x\text{Mn}_{4-x}\text{O}_8$ i.e. spinel solid solutions of the type originally reported by West and co-workers [6]. In this work, we describe the preparation and electrochemical properties of some of the most promising members of this class of material, namely $\text{Li}_2\text{Co}_{0.8}\text{Mn}_{3.2}\text{O}_8$, $\text{Li}_2\text{Fe}_{0.8}\text{Mn}_{3.2}\text{O}_8$ and the double metal ion doped compound $\text{Li}_2\text{Co}_{0.4}\text{Fe}_{0.4}\text{Mn}_{3.2}\text{O}_8$ [7].

2. Experimental

The members of the $\text{Li}_2\text{M}_x\text{Mn}_{4-x}\text{O}_8$ ($x = 0.8$ and $\text{M} = \text{Co}; \text{Fe}$ and CoFe) family were prepared by the dissolution method. Stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ (Fluka), $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (Aldrich), $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Fluka) and $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Aldrich) were dissolved in a solution of H_2O and CH_3COOH . The solutions were stirred and

evaporated to dryness at 120°C . The resulting powders were ground and pre-calcined in air at 200°C for 2 h and at 300°C for 10 h. The solids were crushed and annealed under oxygen flux at 800°C for 24 h with slow-cooling and intermittent regrinding. The chemical composition of the final compounds was determined by plasma atomic emission (ICP) analysis, which confirmed the expected stoichiometry. The structure of the compounds was determined by XRPD analysis (Philips PW Diffractometer with graphite monochromator).

The as-prepared compounds were electrochemically characterized by moulding them in a mixture with 5% of polyvinylidene fluoride (PVDF binder) and 5% of carbon (Super P conductive agent) dissolved in *N*-methyl-2-pyrrolidone. The slurry was then cast onto an Al foil, dried at 80°C under vacuum for 8 h to form films of approximately $300\ \mu\text{m}$ thickness. Disks having $1\ \text{cm}^2$ area and $3\text{--}8\ \text{mg}\ \text{cm}^{-2}$ of active material have been used as electrodes in the testing cells. These were of the button-type with lithium as both the counter and the reference electrode in a 1 M $\text{LiPF}_6\text{--PC}$ (Merck battery-grade) solution. Tests of a complete Li-ion cell have been performed by contacting in sequence a $\text{Li}_2\text{Co}_{0.4}\text{Fe}_{0.4}\text{Mn}_{3.2}\text{O}_8$ -based cathode film, a $\text{LiPF}_6\text{--PC}$ liquid electrolyte soaked in a felt separator and a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based anode film. The latter has been prepared according to [8].

The electrochemical analyses were carried out using an AMEL 2051 potentiostat coupled with an AMEL 568 function generator for the cyclic voltammetry, a Solartron 1255B frequency response analyzer for the electrochemical impedance spectroscopy and a Maccor automatic cycler for the cycling tests.

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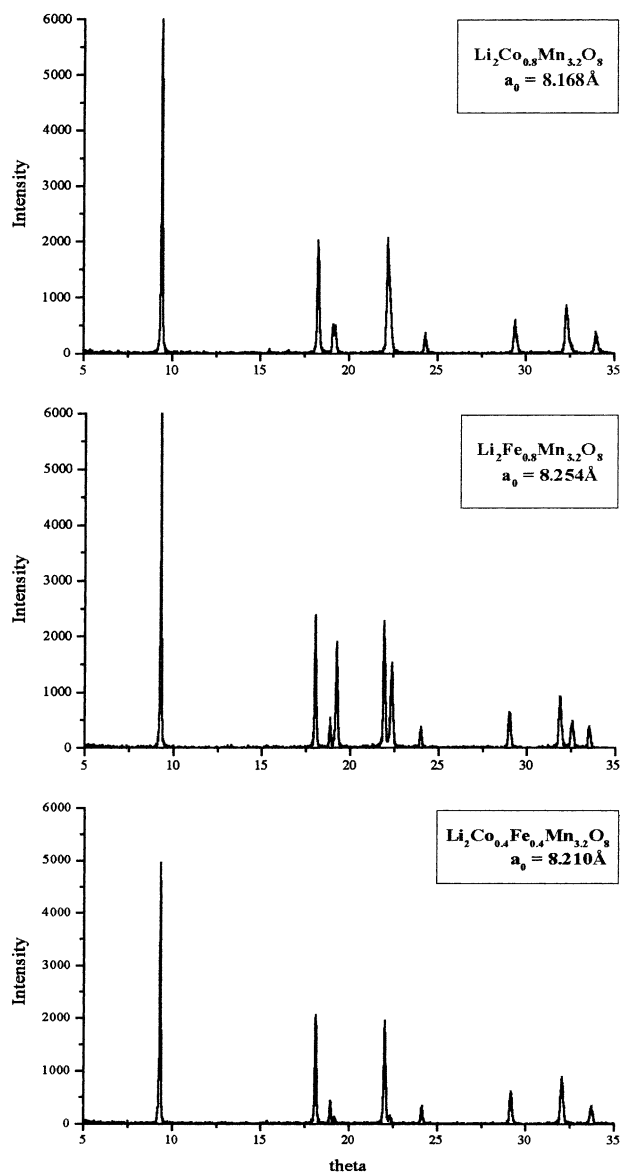


Fig. 1. XRD patterns of the spinels: $\text{Li}_2\text{Co}_{0.8}\text{Mn}_{3.2}\text{O}_8$; $\text{Li}_2\text{Fe}_{0.8}\text{Mn}_{3.2}\text{O}_8$ and $\text{Li}_2\text{Co}_{0.4}\text{Fe}_{0.4}\text{Mn}_{3.2}\text{O}_8$.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns of the $\text{Li}_2\text{M}_x\text{Mn}_{4-x}\text{O}_8$ ($\text{M} = \text{Co}; \text{Fe}; \text{CoFe}$) samples. The patterns, which can be indexed as cubic spinel phase ($Fd\bar{3}m$), reveal a high degree of crystallinity in the samples. All doped materials show similar diffraction patterns, although additional peaks for other phases were observed in $\text{Li}_2\text{Fe}_{0.8}\text{Mn}_{3.2}\text{O}_8$ case. A slight variation in the lattice constant with the doping cations was found when compared with the lattice constant of the stoichiometric spinel LiMn_2O_4 ($a = 8.247 \text{ \AA}$).¹

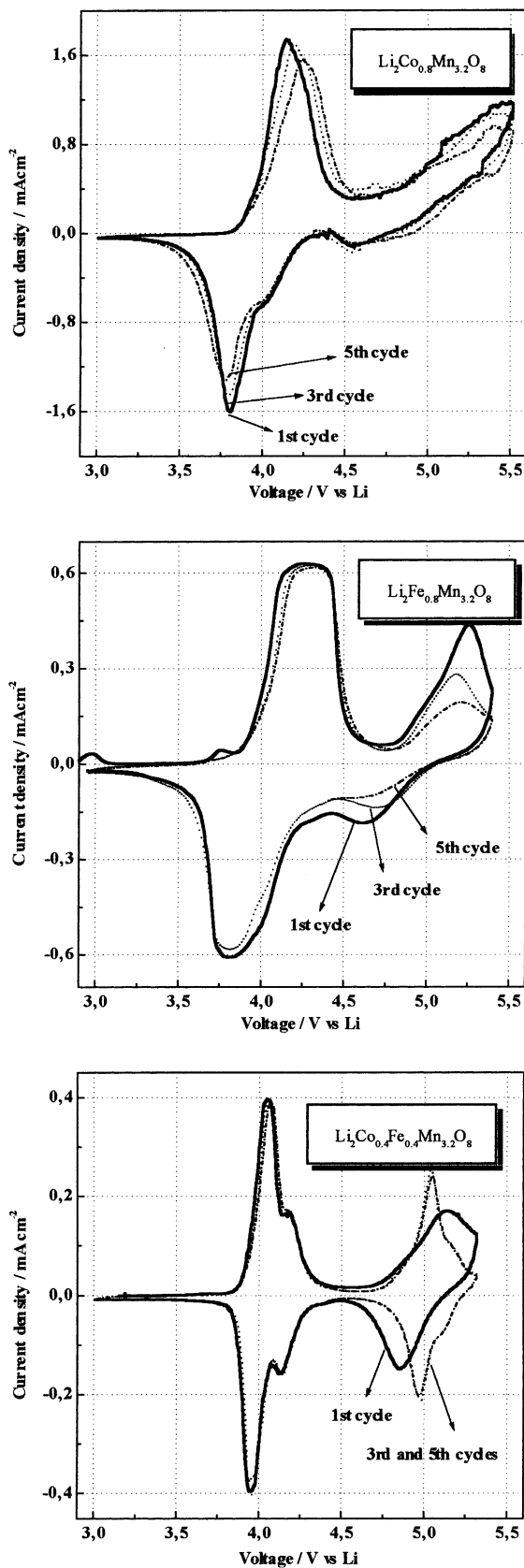


Fig. 2. Cyclic voltammeteries of the spinels in a 1 M LiPF_6 -PC electrolyte cell: Li counter and reference electrode; scan rate 0.1 mV s^{-1} ; room temperature.

¹J.C.P.D.S. 35–782.

Fig. 2 shows the voltammetric response of the three substituted cathode materials, run in cells using Li counter and Li reference electrodes in a 1 M LiPF₆-PC solution. As can be seen, the cobalt, iron and copper-iron containing samples give operating voltage higher than 4.5 V in addition to usual operating voltage around 4.0 V observed for the simple LiMn₂O₄ spinel. Moreover, the Li₂Co_{0.4}Fe_{0.4}Mn_{3.2}O₈-based cell shows improvement of the cycling characteristics of the spinel in the 5 V region. The two voltammetric peaks are highly reversible and well-defined, this suggesting fast kinetics for both electrochemical processes. This is confirmed in Fig. 3, which reports the first charge–discharge cycle profile for the three substituted

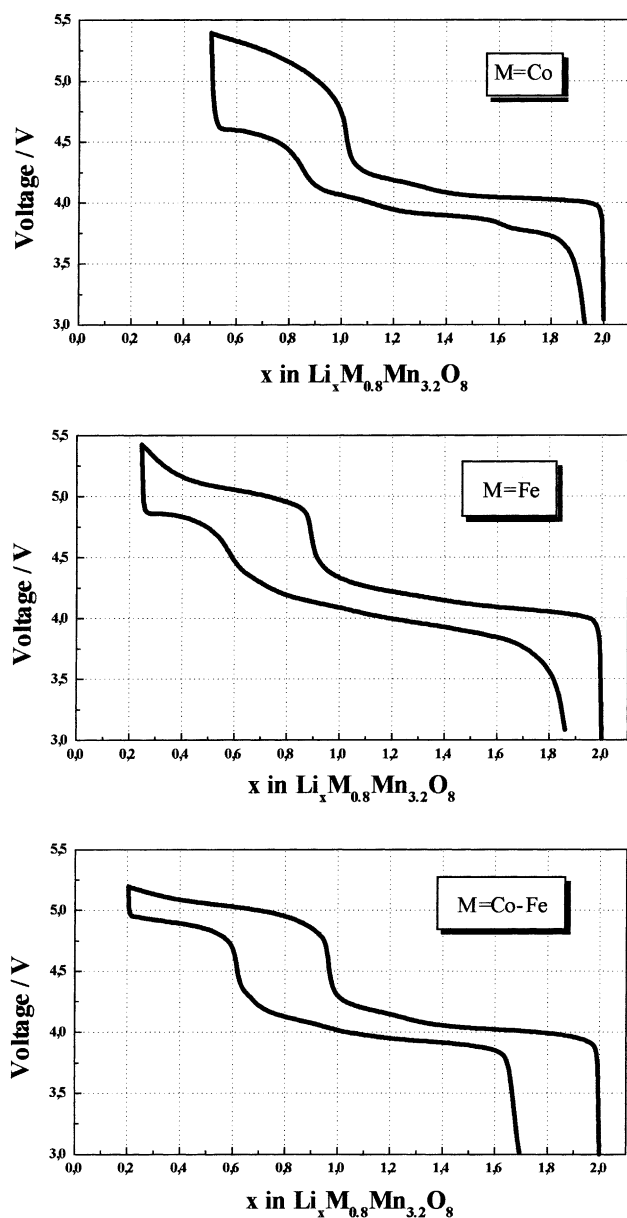


Fig. 3. Potential profiles during the first cycle for Li₂Co_{0.8}Mn_{3.2}O₈; Li₂Fe_{0.8}Mn_{3.2}O₈ and Li₂Co_{0.4}Fe_{0.4}Mn_{3.2}O₈ in a LiPF₆-PC solution: Li counter; current rate C/5; potential limits 3–5.4 V; room temperature.

spinel, recorded at a current rate of C/5 in the 3–5.4 V voltage range. Two well-defined pseudo-plateaux, reflecting the two-step Li deintercalation–intercalation process, characterize the curves. However, the discharge capacity along the higher potential region is clearly lower, the effect of the first cycle being more pronounced for the double metal doped Li₂Co_{0.4}Fe_{0.4}Mn_{3.2}O₈ spinel.

Fig. 4(A) shows the capacity delivery upon cycling. Although reasonably stable, the LiPF₆-PC electrolyte still suffers from decomposition when hold at voltages higher than 5 V. Thus, some decay in capacity for the compounds is observed. However, the results clearly suggest that the Li₂M_xMn_{4-x}O₈-based electrodes may be cycled with a reasonably high capacity, these values being kept even at reasonably high rates, as demonstrated by Fig. 4(B) which reports the cycling capacity delivered at C rate by Li₂Co_{0.4}Fe_{0.4}Mn_{3.2}O₈.

The above characterization leads to the conclusion that Li₂Co_{0.4}Fe_{0.4}Mn_{3.2}O₈ is a cathode of practical interest for use in new-concept lithium-ion batteries. We have confirmed

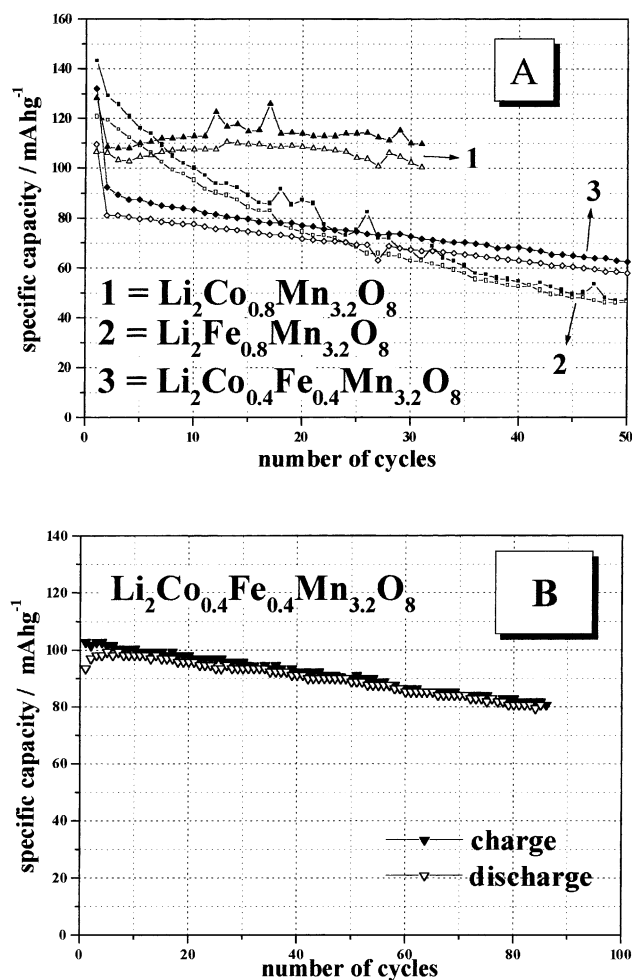


Fig. 4. Capacity delivery upon cycling in a LiPF₆-PC cell: Li counter; potential limits 3–5.4 V; room temperature; (A) galvanostatic charge–discharge capacity at C/5 rate; (B) galvanostatic charge–discharge capacity for the Li₂Co_{0.4}Fe_{0.4}Mn_{3.2}O₈ at C rate.

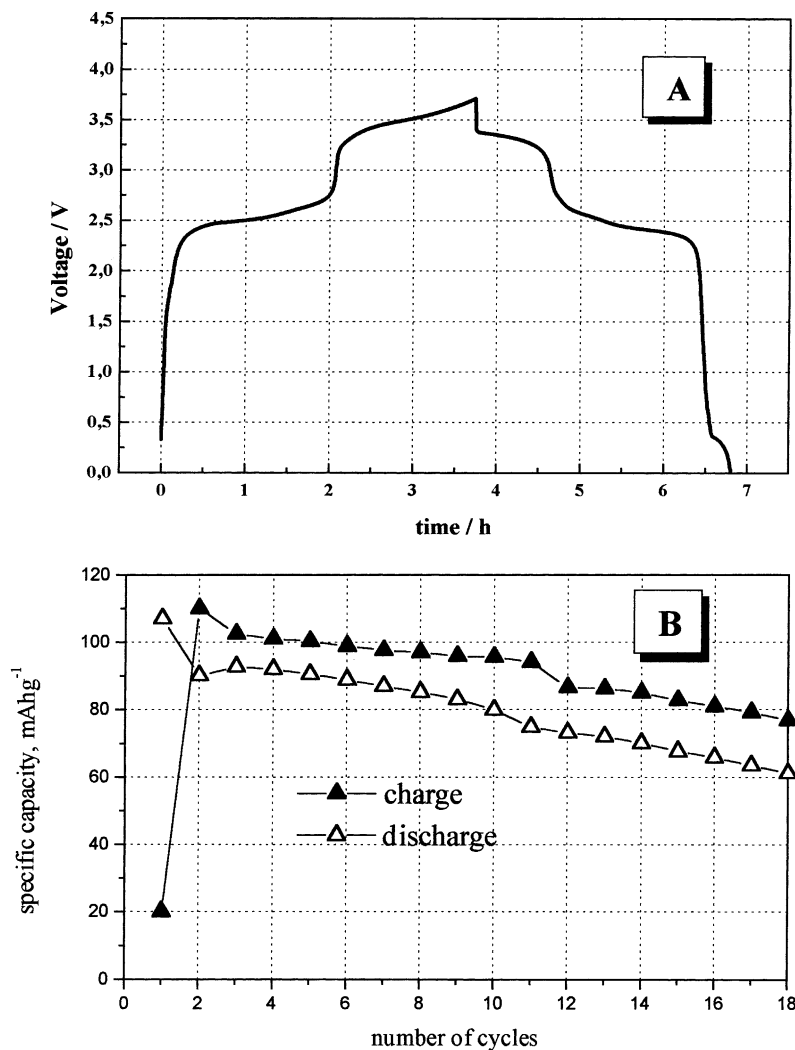


Fig. 5. (A) Typical voltage profile of a charge–discharge cycle of a $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiPF}_6\text{-PC}/\text{Li}_2\text{Co}_{0.4}\text{Fe}_{0.4}\text{Mn}_{3.2}\text{O}_8$ lithium-ion cell. Cycling rate 0.1 mA cm^{-2} ; (B) capacity delivery upon cycling of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiPF}_6\text{-PC}/\text{Li}_2\text{Co}_{0.4}\text{Fe}_{0.4}\text{Mn}_{3.2}\text{O}_8$ lithium-ion cell. The capacity is referred to the $\text{Li}_2\text{Co}_{0.4}\text{Fe}_{0.4}\text{Mn}_{3.2}\text{O}_8$ cathode.

this by coupling it with a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material, also developed in our laboratory [8] and a $\text{LiPF}_6\text{-PC}$ electrolyte. Fig. 5 shows a typical charge–discharge cycle which demonstrates the operation of the cell in the expected 3 V region.

4. Conclusion

Doped electroactive $\text{Li}_2\text{M}_{0.8}\text{Mn}_{3.2}\text{O}_8$ spinels have been prepared and evaluated in Li cells. The results show that lithium can be extracted from the spinel structures over two main potential regions: i.e. 3.9–4.4 and 4.5–5.2 V. The upper voltage depends on the nature of the metal ion M, the Fe-based spinels giving the highest capacity. At the same time, the reversibility upon cycling in the 5 V region increases with the use of the double metal doped $\text{Li}_2\text{Co}_{0.4}\text{Fe}_{0.4}\text{Mn}_{3.2}\text{O}_8$ oxide. Indeed, the Co–Fe doping seems to have a synergetic effect on the improvement of the cycling life, which may represent the first step to the real application

of 5 V cathode materials in the future-design, high-energy Li-ion batteries.

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