

Doped Li–Mn Spinels: Physical/Chemical Characteristics and Electrochemical Performance in Li Batteries

G. Pistoia,* A. Antonini, and R. Rosati

*Centro di Studio per la Elettrochimica e la Chimica Fisica delle Interfasi, CNR,
Via Castro Laurenziano 7, 00161 Rome, Italy*

C. Bellitto and G. M. Ingo

*Istituto di Chimica dei Materiali, CNR, Area della Ricerca di Roma,
00016 Monterotondo Stazione, Rome, Italy*

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Several doped spinel-type Li–Mn oxides of formula $\text{Li}_{1+x}\text{M}_y\text{Mn}_{2-(x+y)}\text{O}_{4+z}$, where Mn is partly replaced by Li, Cu, Zn, Ni, Co, Fe, Cr, Ga, Al, B, or Ti, were prepared by a solid-state reaction at 730 °C. These spinels were investigated by X-ray powder diffraction, thermal analysis, slow step voltammetry, and galvanostatic cycling at medium-high rates. Even substitutional levels as low as 0.05 atom/formula unit produce structural effects that are reflected in the electrochemical characteristics. The substituents may occupy either tetrahedral 8a sites or octahedral 16d sites. Examples of the first type of substitution are provided by Ga^{3+} and Zn^{2+} , while octahedral sites are preferred by, e.g., Ni^{2+} and Cr^{3+} . Cycling at practical rates produces capacities of ~ 100 mA h/g for the best materials with limited capacity losses ($3\text{--}6 \cdot 10^{-2}$ mA h/g·cycle). The lower Mn^{3+} content with respect to undoped spinel explains the initially lower capacities.

Introduction

In the past few years, investigations aimed at replacing LiCoO_2 with LiMn_2O_4 in practical Li-ion batteries have been quite active. The advantages of Mn spinels are well-known¹ and so are main disadvantages: a relatively low capacity (~ 120 mA h/g) and fading upon cycling. For some applications, and taking into account the positive aspects, a capacity of 100–110 mA h/g would be acceptable, provided it could be stabilized under extended cycling.

With this aim in mind, several groups have tried to improve spinel cyclability by partly substituting Mn^{3+} with different ions. The main cause for the capacity loss was judged to be the change of cubic symmetry into a tetragonal one (Jahn–Teller effect) occurring at high reduction levels.^{2,3} An increase of the Mn oxidation state above 3.5 was sought to reduce this effect.^{2,3} In early studies, monovalent (Li) and divalent (Zn, Mg, Cu, Ni) ions have been preferred to this end.^{2–6} Subsequently, trivalent ions (mostly of the transition elements, such as Co and Cr) have been tested with a view to replacing Mn^{3+} in 16d octahedral sites without causing strains in the structure.^{7–9}

It seems that, up to now, little attention has been paid to the type of sites occupied by the substituting ions. Possible occupancy of tetrahedral sites was not seen as favorable.⁹ Furthermore, the possibility that covalent bonds could be formed by these ions¹⁰ was not taken into account to help identify site occupancy.

In this paper, a number of substituents have been considered. Their oxidation states range from +1 to +4, and they can occupy either tetrahedral or octahedral sites, forming ionic or covalent bonds. The electrochemical behavior of the different spinels was examined potentiostatically at low rate (10 mV/1 h) and galvanostatically at medium-high rates (1–3 mA/cm²), to try to find a correlation with structural features.

Experimental Section

Sample Preparation. The following substituents, M, have been studied: Li, Cu, Zn, Ni, Co, Fe, Cr, Ga, Al, B and Ti. A typical synthesis was carried out at the following conditions: Li_2CO_3 , MnO_2 (CMD from Sedema, Belgium), and a salt (usually the M oxide) of the substituent were mixed so to produce a nominal composition $\text{Li}_{1.02}\text{M}_{0.05}\text{Mn}_{1.95}\text{O}_4$. The components were ball-milled for 1 h and then transferred to an oven, where they were left 72 h in the air at 730 °C. Slow cooling was always applied (24 h).

Ni- and Co-doped spinels were also synthesized in alternative conditions, by using divalent salts (NiO and $\text{Co(II)-acetylacetonate}$, respectively) under a N_2 stream. The Ti-

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Table 1. Elemental Analysis Results for Selected Spinel

nominal composition	Li/Mn	Mn oxidation state	Mn ³⁺ (atom/mol)	composition as Li _a Mn _b O _c	M/Mn ^a
Li _{1.02} Mn ₂ O ₄	0.53	3.60	0.78	Li _{1.05} Mn _{1.95} O _{4.04}	
Li _{1.02} Zn _{0.05} Mn _{1.95} O ₄	0.54	3.62	0.74	Li _{1.05} Mn _{1.95} O _{4.05}	
Li _{1.02} Ga _{0.05} Mn _{1.95} O ₄	0.55	3.62	0.74	Li _{1.07} Mn _{1.93} O _{4.03}	0.027
Li _{1.02} Ti _{0.05} Mn _{1.95} O ₄	0.54	3.57	0.83	Li _{1.06} Mn _{1.94} O _{4.00}	0.027

^a Nominal ($M = 0.05$, $Mn = 1.95$): 0.026.

doped spinel was prepared using Ti powder. Some samples were also prepared with larger amounts of M, e.g., 0.1, 0.25, or 0.5 atom/LiMn₂O₄ unit.

Chemical Analysis. For Li_{1.02}Mn₂O₄ and three substituted spinels ($M = Zn, Ga$ and Ti), the composition, expressed as Li_aMn_bO_c, was determined by Sedema Laboratories. Li was found as Li₂O by inductively coupled plasma (ICP). Total Mn was determined by completely dissolving the spinel in HCl, followed by potentiometric titration of Mn²⁺ by KMnO₄ in the presence of Na pyrophosphate. The average Mn oxidation state was found by reacting the sample with excess ammonium ferrous sulfate, to reduce all manganese to Mn²⁺, and back-titrating Fe²⁺ with KMnO₄. For Ti- and Ga-doped spinels, the analyses were also carried out by Malissa and Reuter Laboratories (Germany). In this case, the M/Mn ratio was particularly sought.

Physical Measurements. Thermal gravimetry (TG) and differential thermal analyses (DTA) were obtained in air using a computer-controlled Stanton Redcroft STA-781 thermal analyzer at the heating rate of 10 °C/min.

X-ray diffraction patterns (XRD) were recorded by multiple scanning on an automated Seifert XRD-3000 diffractometer (flat plate sample, curved graphite single-crystal monochromator [Cu Kα = 1.542 Å], position-sensitive detector) operating in a constant scan mode at 0.5° min⁻¹ over the range 3° < 2θ < 80°. The phase identification (i.e., *Fd3m* space group) and the evaluation of the lattice parameter *a* of the spinel were carried out by using Seifert XDAL 3000 Software Index I.

Electrochemical Studies. For the electrochemical tests, the samples were mixed with acetylene black and Teflon. A 10 mg sample of cathodic mixture contained 7 mg of spinel, 2 mg of acetylene black, and 1 mg of Teflon. This composite was pressed into a pellet on an Al net at 9 tons/cm². Coin cells were assembled with these cathodes, Li anodes, and a LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) solution supported on a glass wool separator. To avoid corrosion of the stainless steel case at the high potentials reached during charging (up to 4.4 V), the cathode material and the case were in contact only through a shank of the Al exmet.

Two types of electrochemical tests were run: potential step voltammetry and galvanostatic cycling. The first experiments were carried out with a MacPile II potentiostat/galvanostat. The cathodes were submitted to potentials steps of 10 mV/1 h up to 4.4 V and then discharged in the same way to 3.5 V. With this slow voltammetry technique, quasi-equilibrium conditions are achievable which can yield thermodynamic information. In one experiment, an unsubstituted spinel was compared with Li_{1.02}Ga_{0.05}Mn_{1.95}O₄ at the higher rate of 12.5 mV/0.036 h (100 μV/s) to determine different rate capabilities.

The cycling tests were run, with an Arbin battery test system, at the relatively high current of 1 mA/cm², during both charging and discharging, corresponding to a 1 h rate (V limits: 4.35–3.50 V). In a comparison of the rate capability of samples of nominal compositions Li_{1.05}Mn₂O₄, Li_{1.07}Mn_{1.95}O₄ and Li_{1.02}Ga_{0.05}Mn_{1.95}O₄, cycling was performed with the following procedure: discharge, 3 mA/cm²; charge, 1 mA/cm².

Results and Discussion

Structure and Composition of Substituted Spinel. A screening of literature data on the cathodic performance in Li cells of substituted spinels^{5–9,12} shows some disagreement on the effectiveness of the single

substituents and on the capacity values attainable. This may be the result of the frequent lack of chemical analysis on the samples used.

Especially if the synthesis is carried out using MnO₂ as a Mn source and the temperature is kept at 700–750 °C, the following departures from the expected composition may result: (1) Li/Mn ratios higher than 0.5 (or the value selected) since the amount of MnO₂ in the starting material (CMD) is less than 100%,¹³ (2) lower Mn content than 2 in LiMn₂O₄; (3) possible formation of other phases, such as Li₂MnO₃.

On the basis of these ideas, X-ray data revealing other phases (within the sensitivity limits of the technique) and chemical analysis aimed at determining the real Li/Mn and Mn³⁺/Mn⁴⁺ ratios are necessary. If LiMn₂O₄ is accompanied by impurities (e.g., Li₂MnO₃ or LiMnO₂), its initial capacities can be higher than that delivered by a truly Li-rich spinel of the type Li_{1+x}M_yMn_{2-x}O₄.¹⁴ This apparent paradox might explain some capacity values for substituted spinels which are even higher than the theoretical ones. Values of 120 mA h/g, or higher, with contents of foreign ions M of 0.1 atom/mol or more, in Li_{1+x}M_yMn_{2-(x+y)}O_{4+z} may be explained only by the presence of impurities.

We have analyzed some samples, with or without M, to find their real composition, and the results are reported in Table 1. The electrochemical potentials for the reduction of the substituents of Table 1 are such that they do not take part in the redox reactions used to determine Mn and MnO₂ (see Experimental Section).

The experimental M/Mn ratios for Ti- and Ga-doped spinels are close to the nominal one. This enables us to exclude the presence of foreign phases based on unreacted M. From the Mn oxidation state the amount of Mn³⁺, which determines the theoretical capacity, was calculated. In the undoped stoichiometric spinel LiMn₂O₄, with Mn³⁺ = 1 atom/mol, a theoretical capacity of 148 mA h/g may be calculated. Accordingly, one obtains 114 mA h/g for Li_{1.02}Mn₂O₄ (Mn³⁺ = 0.78 atom/mol) and capacities in the range 109–123 mA h/g for the substituted spinels. The capacity decreases as the (Li + M)/Mn ratio increases and the valence of M decreases, as less Mn³⁺ is required for electroneutrality. In general, one has to be rather cautious when dealing with reported practical capacities of more than 100 mA h/g, especially if the substitutional level is high.

The X-ray analysis shows that with low substituent levels, e.g., 0.05 atom/mol, no other phases can be detected, while higher levels may produce other detect-

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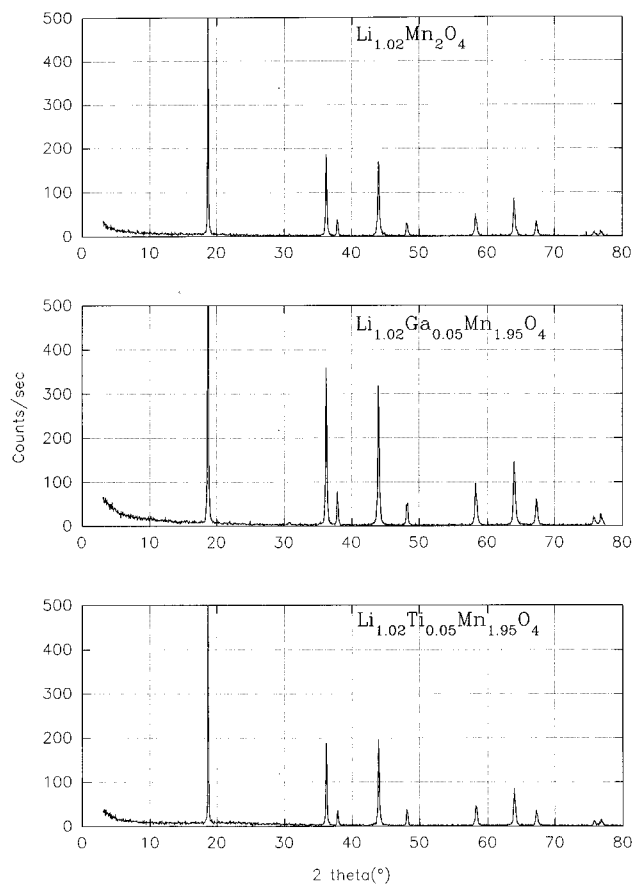


Figure 1. X-ray diffractograms of spinels of nominal compositions: $\text{Li}_{1.02}\text{Mn}_2\text{O}_4$; $\text{Li}_{1.02}\text{Ga}_{0.05}\text{Mn}_{1.95}\text{O}_4$; $\text{Li}_{1.02}\text{Ti}_{0.05}\text{Mn}_{1.95}\text{O}_4$.

able phases in addition to spinel. In Figure 1, the X-ray patterns of nominal $\text{Li}_{1.02}\text{Mn}_2\text{O}_4$, $\text{Li}_{1.02}\text{Ti}_{0.05}\text{Mn}_{1.95}\text{O}_4$, and $\text{Li}_{1.02}\text{Ga}_{0.05}\text{Mn}_{1.95}\text{O}_4$ are shown. They are identical, and their cubic parameter a is also very similar: 8.225(1) Å. Some spinels with general nominal formula $\text{Li}_{1.02}\text{M}_x\text{Mn}_{2-(x+y)}\text{O}_{4+z}$ were also analyzed ($M = \text{Cr}, \text{Co}, \text{Ti}, \text{Ga}, \text{and Fe}$). As shown in Figure 2, the Ti-doped spinel has a single-phase pattern (as also found for the Cr-doped spinel). With the Ga-doped spinel (and with the similar Co-doped spinel) small extra peaks appear at 31° , 37° , and 45° . The latter two peaks indicate formation of Li_2MnO_3 . The Fe-doped spinel has small extra peaks at 35.5° , 45° , and 57.5° : at least another phase, in addition to Li_2MnO_3 , is present.

The patterns of Figure 2 indicate that the spinel $\text{Li}_{1+x}\text{M}_y\text{Mn}_{2-(x+y)}\text{O}_{4+z}$ is still the only or predominant phase even at $M = 0.25$, but some new phases may appear, either from an intrinsic process or as a consequence of inadequate precursor mixing.

In Table 2, the a parameter of different spinels with $M = 0.25$ is reported, along with the ionic radii of M . The higher a value for the $M = \text{Ti}$ and the lower for $M = \text{Co}$, with respect to M -free spinel, agree with literature data.^{8,15} As shown in Table 2, no definite correlation exists between ionic radius and a . As an example, Ga^{3+} and Cr^{3+} have the same radius but give spinels with rather different a . It is clear that one should consider not only the radius but also other factors, such as site of insertion and possible formation of covalent bonds.

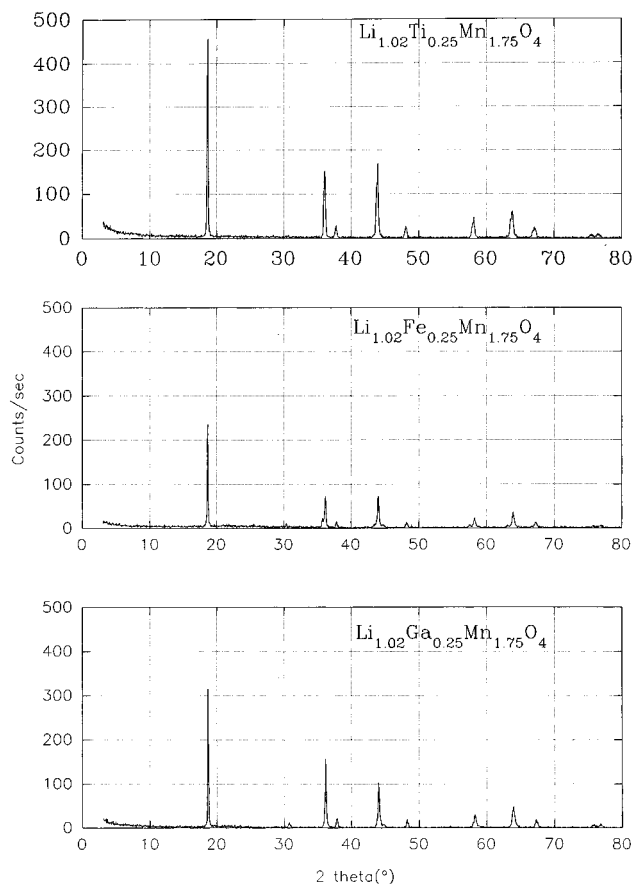


Figure 2. X-ray diffractograms of spinels of nominal formula $\text{Li}_{1.02}\text{M}_{0.25}\text{Mn}_{1.75}\text{O}_4$.

Table 2. Ionic Radii of Selected Ions and Cubic Parameter for $\text{Li}_{1.02}\text{M}_{0.25}\text{Mn}_{1.75}\text{O}_4$

M (0.25 atom/mol)	r_M (Å) ^a	a (Å)
Ga	0.62	8.224(1)
Fe	0.55 ls/0.65 hs	8.227(1)
Co ^b	0.55 ls/0.61 hs	8.206(1)
Cr	0.62	8.205(1)
Ti	0.61 ^c	8.237(1)
Mn	0.65 hs	8.225(1)

^a Data from Shannon,²⁸ based on $r_{\text{O}_2} = 1.40$ Å. ^b Synthesis in the air (Co^{3+} assumed). ^c Other authors report for Ti^{4+} values of 0.64 Å,¹⁰ 0.68 Å,¹⁵ or 0.75 Å.⁸

In Table 3, the substituents used in this work are listed together with (1) the octahedral site preference energy,¹⁶ (2) the preferential coordination if covalent bonds are formed,¹⁰ and (3) the ionic radii. The first has been derived for spinels on the basis of the Madelung constant, short-range energy, and crystal field energy. The second specifically addresses the formation of hybrid covalent bonds, together with the related geometry and bond strength. It can be noted that (1) most of the cations prefer a tetrahedral coordination (negative energy values), (2) there is an excellent agreement between the site preference and the geometry of moderate or strong covalent bonds, with the exception of Cu^{2+} , (3) the latter prefers octahedral sites as it is further stabilized there by the Jahn–Teller effect,¹⁷ and (4) Li^+ and Al^{3+} can form only ionic bonds,

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Table 3. Octahedral Site Preference Energies of Various Ions and Occurrence of Covalent Bonds

substituent	O.S. preference energy ^a (kJ/g atom weight)	covalent preferential coordination ^b	ionic radius ^c
Li ⁺	-15.0		0.73
Cu ²⁺ (d ⁹)	-0.42	sq pl (dsp ²), strong; tet (sp ³), mod	0.73
Co ²⁺ (d ⁷)	-43.9		0.65 ls, 0.75 hs
Zn ²⁺ (d ¹⁰)	-31.6	tet, strong	0.74
Ni ²⁺ (d ⁸)	37.6	sq pl, mod	0.69
Co ³⁺ (d ⁶)			0.55 ls, 0.61 hs
Ni ³⁺ (d ⁷)			0.56 ls, 0.60 hs
Al ³⁺	-10.5		0.57
Ti ³⁺ (d ¹)	-91.5		0.67
Ti ⁴⁺ (d ⁰)		tet, mod	0.61
Cr ³⁺ (d ³)	69.4	oct (d ² sp ³), mod	0.62
Mn ³⁺ (d ⁴)	13.0	sq pl, strong	0.65
Fe ³⁺ (d ⁵)	-55.6	tet, mod	0.55 ls, 0.65 hs
Ga ³⁺ (d ¹⁰)	-64.4	tet, mod strong	0.62

^a From ref 16. More positive values represent preference for the octahedral 16d spinel sites. ^b From ref 10. When covalent bonds are thought to occur, the coordination and the bond strengths are indicated. Sq pl = square planar, tet = tetrahedral, oct = octahedral. Square bonds are formed by d⁴, d⁸ and d⁹ cations accommodated in an octahedral site. ^c According to Shannon.²⁸

Table 4. DTA Peaks of Substituted and Unsubstituted Spinel

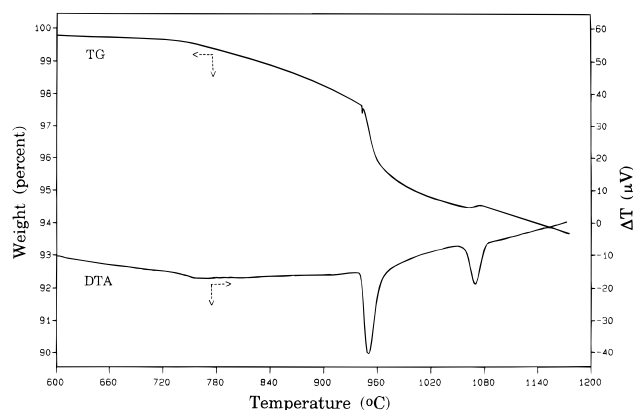
nominal composition	1st peak (°C)	2nd peak (°C)
Li _{1.02} Mn ₂ O ₄	947.4 ^a	1076.5 ^a
Li _{1.04} Mn ₂ O ₄	946.3	1075.9
Li _{1.05} Mn ₂ O ₄	945.4	1075.3
Li _{1.02} Ga _{0.05} Mn _{1.95} O ₄	951.0	1072.2
Li _{1.02} Co _{0.05} Mn _{1.95} O ₄	936.8	1072.6

^a A decimal figure is reported, this being the precision of the instrument's thermocouple.

and Co²⁺, Co³⁺, Ni³⁺, and Ti³⁺ can form only weak covalent bonds.¹⁰

Table 3 suggests that many substituents may replace Li⁺ in the tetrahedral 8a sites and displace the latter in octahedral 16d sites. In a recent study, it has been shown that these sites are different from the 16d octahedral sites occupied by Mn.¹⁸ The possible occurrence of spinels of the type (Li_{1-y}M_y)_t(Li_{x+y}Mn_{2-(x+y)})_oO_{4+z} was not seen in the literature as a favorable event. Therefore, cations which were thought to replace Mn³⁺ in its sites, as Cr³⁺, were preferentially examined.⁹ We shall show in the following that also cations entering the tetrahedral sites can have a stabilizing effect on the spinel structure.

Thermal Behavior. In a preliminary study of the thermal behavior of M-doped and undoped spinels, we have examined the compounds listed in Table 4. The TG/DTA curves of one of them, the Ga-doped spinel, are reported in Figure 3 (the curves for the other samples are qualitatively the same). The TG curve shows some clear features: (1) evident changes in the slope at ~740 °C and at ~940 °C; (2) a very small weight gain at ~1070 °C. The features of point (1) have already been stressed in ref 4 for samples in the series Li_{1+x}Mn_{2-x}O₄. The slope change at ~740 °C is due to oxygen loss and does not correspond to any 1st-order transition, as also evidenced by the lack of a peak in the DTA curve. Instead, the second slope change corresponds to a peak

**Figure 3.** DTA and TG curves for Li_{1.02}Ga_{0.05}Mn_{1.95}O₄. 10 °C/min, air.

(1st-order transition), and it is due to a further oxygen loss leading to a new phase. In a similar experiment,¹⁹ this new phase was identified as the tetragonal spinel LiMn₂O_{3.84}. The small weight gain at ~1070 °C is also a 1st-order phase transition (peak in the DTA curve), but we cannot determine at the moment which new phase is formed.

The DTA peaks referred to unsubstituted spinels (Table 4) are in very good agreement with the data reported in ref 20. From Table 4, one may see that the 2nd peak in the DTA curve is practically invariant. Instead, the 1st peak shows a higher value for Ga³⁺ and a lower one for Co³⁺ with respect to the three Li_{1+x}Mn₂O₄ samples, whose values are constant as found in ref 4 for similar samples. Although preliminary in nature, these experiments seem to indicate that substitution in the tetrahedral sites (Ga³⁺) may even contribute to stabilize the structure. As for Co³⁺, which is supposed to occupy octahedral sites,^{17,21} it seems to favor oxygen loss (~937 °C vs ~947 °C for nominal Li_{1.02}Mn₂O₄).

Electrochemical Tests: Slow Step-Voltammetry.

To try to have more information on the effect of substituents on the structure stabilization, electrochemical tests were carried out. Slow step voltammetry affords reversible insertion/deinsertion of Li⁺ in the spinel structure in quasi-equilibrium conditions.²² The chosen rate of 10 mV/1 h corresponds, in a continuous scan of cyclic voltammetry, to 2.8 μV/s. In Figures 4 and 5, the results related to five substituted spinels are reported together with those of the M-free one. ΔQ in Figure 4 is the capacity (mA h) involved in each potential step and corresponds to the change of Li⁺ concentration in the step (ΔC_{Li⁺}/10 mV). The plots of Figure 4 are differential plots similar to the dx/dV vs V ones.^{22,23} The final parts of the anodic curves reveal irregularities connected with electrolyte decomposition.

Even at the low substitutional level of 0.05 atom/mol, changes are induced into the ΔQ/V profile of pristine Li_{1.02}Mn₂O₄. In Li_{1.07}Mn_{1.95}O₄, the height of both peaks

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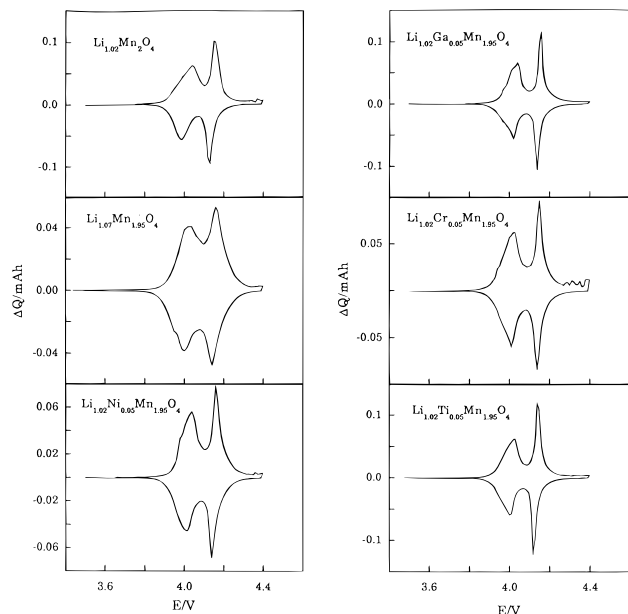


Figure 4. $\Delta Q/V$ plots for different spinels. ΔQ is the capacity variation (mAh) in the 10 mV step.

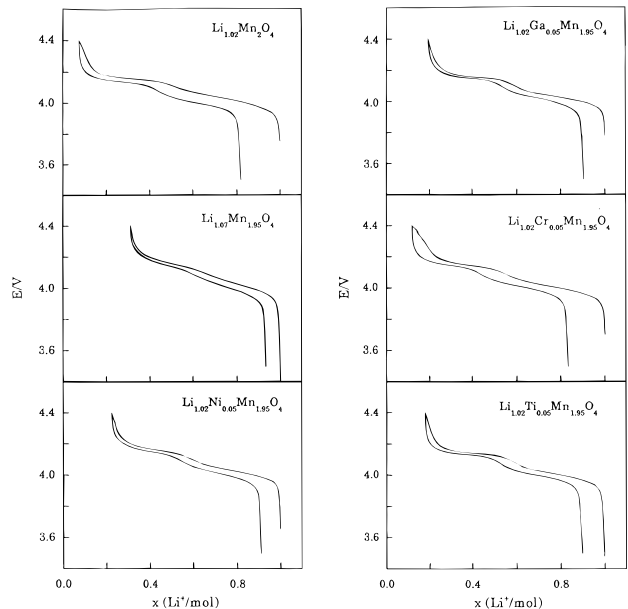


Figure 5. V/x plots for different spinels. For simplicity, all materials were assumed to have initially 1 Li⁺/mol. Potentiostatic conditions, 10 mV/1 h.

is decreased, in agreement with the results in ref 24 for the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ series ($0.04 < x < 0.20$). In the above reference, the two peaks and the minimum between them have been attributed to the sequence disorder–order–disorder occurring upon Li⁺ deinsertion. The presence of excess Li⁺ in the octahedral 16d sites would have a pinning effect over Li⁺ in the tetrahedral 8a sites. As a consequence, the latter ions would be less free to move in the 8a sublattice, thus rendering less evident ordering effects. Eventually, for $x = 0.20$ the two peaks are barely discernible.²⁴ In the Ni-, Ga-, Ti-, and Cr-doped spinels, peak smoothing is much less evident. According to Table 3, Ga³⁺ and Cr³⁺ occupy tetrahedral and octahedral sites, respectively (these data are not available for Ni³⁺ and Ti⁴⁺). This

Table 5. Results from Step Voltammetry Tests at 10 mV/1 h (V limits: 4.40–3.50 V) for Spinels of Nominal Composition $\text{Li}_{1.02}\text{M}_{0.05}\text{Mn}_{1.95}\text{O}_4$ (Capacities from Galvanostatic Discharges Enclosed for Comparison)

substituent (M)	1st discharge capacity (mA h/g)		theoretical capacity (mA h/g) ^a	ΔV_1 (mV)	ΔV_2 (mV)
	step voltammetry	cycling ^b			
none	109		114	52	24
Li	92	92		24	24
Zn	98	95	109	29	19
Ni (air)	102	102		14	20
Ni (N ₂)	105	102		24	11
Co (air)	110	109		19	15
Co (N ₂)		103			
Ga	106	106	109	19	20
Cr	107	102		15	10
Ti	109	109	123	22	17

^a From the Mn³⁺ content (Table 1). ^b At 1 mA/cm².

means that occupation of either site may still maintain, with appropriate ions, a disorder–order–disorder transition. Occupancy of the tetrahedral sites by Ga³⁺, and consequent shifting of Li⁺ into octahedral sites, would in principle produce the same effect observed in $\text{Li}_{1.07}\text{Mn}_{1.95}\text{O}_4$. However, Li⁺ pinning is not evident in this case.

In Figure 5, the V/x profiles for the same spinels of Figure 4 are presented. The following features may be noticed: (1) the kink at ~ 4.1 V on charge is barely visible in $\text{Li}_{1.07}\text{Mn}_{1.95}\text{O}_4$, in accordance with the data of Figure 4; (2) the charge/discharge separation (ΔV) is reduced in all substituted spinels with respect to $\text{Li}_{1.02}\text{Mn}_2\text{O}_4$. This suggests a lower strain upon Li⁺ deinsertion; (3) the level of Li⁺ extracted is below 0.8 atom/mol (with the apparent exception of the Cr-doped spinel, but this is due to a larger electrolyte decomposition; see Figure 4) for all substituted spinels, while for $\text{Li}_{1.02}\text{Mn}_2\text{O}_4$ it is above 0.9 atom/mol.

In Table 5, the 1st-discharge capacities of several spinels, obtained by step voltammetry, are reported and compared with the ones obtained in galvanostatic cycling. The agreement is noteworthy despite the different time scale. This shows the good rate capability of these spinels. In the same Table, the voltage difference between the 1st anodic peak (Figure 4) and its cathodic counterpart (ΔV_1) and between the 2nd anodic/cathodic couple (ΔV_2) are also reported. Remarkable features are (1) $\text{Li}_{1.02}\text{Mn}_2\text{O}_4$, with a theoretical capacity of 114 mA h/g, delivers 109 mA h/g, (2) $\text{Li}_{1.07}\text{Mn}_{1.95}\text{O}_4$, whose real composition was extrapolated to $\text{Li}_{1.11}\text{Mn}_{1.89}\text{O}_{4.03}$, provides a capacity corresponding to the theoretical one, 92 mA h/g, (3) the Ni-doped spinel is likely to have Ni²⁺ when prepared in air or N₂ (see further discussion below), (4) the Co-doped spinel in air is likely to have a large amount of Co³⁺ (high initial capacity also on cycling) and (5) the ΔV_1 and ΔV_2 of all substituted spinels are lower than those of nominal $\text{Li}_{1.02}\text{Mn}_2\text{O}_4$. The last piece of evidence is of some importance. At the 10 mV/1 h rate of potential change (2.8 $\mu\text{V/s}$ in a continuous analogue V sweep) kinetic effects are not that relevant, so the peak separation seems more of a thermodynamic nature. In other words, Li⁺ extraction may have caused different and reduced degrees of structural alterations as a function of the substituent. These correspond to the lattice instability in the charged state, due to the high amount of Li⁺ removed, as discussed in ref 25.

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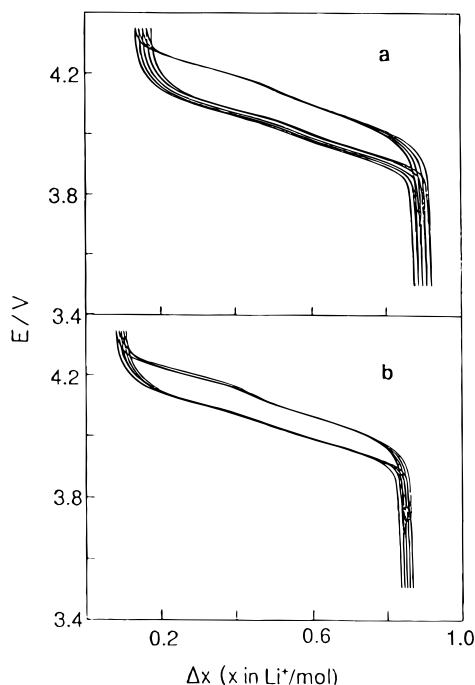


Figure 6. $V/\Delta x$ plots for (a) $\text{Li}_{1.02}\text{Mn}_2\text{O}_4$ and (b) $\text{Li}_{1.02}\text{Ga}_{0.05}\text{Mn}_{1.95}\text{O}_4$. Cycles 21–25. Potentiostatic conditions, 12.5 mV/0.036 h.

Table 6. Capacity Losses at Different Cycle Ranges for the Spinels of Figure 7 (Plus Ni-Doped Spinel in Air and Co-Doped Spinel under N_2)

substituent	capacity loss [(mA h/g cycle)·10 ⁻²]		
	cycles 1–60	cycles 1–150	cycles 60–150
Li ($\text{Li}_{1.05}\text{Mn}_2\text{O}_4$)	22	12	6.6
Li ($\text{Li}_{1.07}\text{Mn}_{1.95}\text{O}_4$)	5.3		
Ni (N_2)	6.5	8.6	9.9
Ni (air)	5.8		
Ga	7.3	5.6	4.5
Ti	10	6.2	3.3
Co (N_2)	5	5.9	6.3
Co (air)	13	9.4	7.0

To have information on possible kinetic differences in the Li^+ deinsertion/insertion processes, a faster step voltammetry was run for two spinels— $\text{Li}_{1.02}\text{Mn}_2\text{O}_4$ and $\text{Li}_{1.02}\text{Ga}_{0.05}\text{Mn}_{1.95}\text{O}_4$. Cycles 21–25 of these tests are shown in Figure 6: the difference in both the charge/discharge ΔV and in the capacity fade can easily be seen. Even this limited substitutional level may have a positive effect on Li^+ diffusion in the 8a–16c–8a paths.

Electrochemical Tests: Cycling. To obtain further insight into the electrochemical behavior of substituted spinels, several cycling tests were carried out. The results are presented in Figures 7–9 and in Tables 6–7. In Figure 7, the compositions $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ and $\text{Li}_{1.07}\text{Mn}_{1.95}\text{O}_4$ are compared with the Ga-, Ti-, Co-, and Ni-doped spinels. The Co-doped spinel was prepared in air (from Co_3O_4) and the Ni-doped spinel under N_2 (from NiO). The Ti- and Ga-doped spinels have satisfactory capacity values and retention upon cycling (see also Table 6). $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ and $\text{Li}_{1.07}\text{Mn}_{1.95}\text{O}_4$ clearly show that the Li/Mn ratio has to be sufficiently high to ensure capacity retention. On the other hand, the latter compound has, at the 50th cycle, a capacity of 90 mA h/g vs 103 mA h/g for the Ti- and Ga-doped spinels. This capacity penalty seems too high for many applications.

To check if metal substitution had affected the conductivity, impedance tests were run on Ti- and Ga-doped spinels and compared with an undoped spinel. For the latter, a resistance of 1.8 Ω cm was measured, which slightly increased to 3.0 Ω cm for $M = \text{Ti}$ and to 4.0 Ω cm for $M = \text{Ga}$. Conductivity clearly does not determine the different performance of these spinels.

The capacity order for spinels of the same formula $\text{Li}_{1.02}\text{M}_{0.05}\text{Mn}_{1.95}\text{O}_4$ is, from Figure 7, $\text{Ti} \sim \text{Ga} \sim \text{Co} > \text{Ni} > \text{Li}$ (with some decrease for Co above 100 cycles with respect to Ga and Ti).

In substituted spinels, the electroneutrality rule suggests the general formula

$\text{Li}[\text{M}^{n+}_x\text{Mn}^{3+}_{1+(n-4)x}\text{Mn}^{4+}_{1-(n-3)x}]\text{O}_4$. From this formula, one recognizes that the lower the valence of the substituent the lower the Mn^{3+} content and, therefore, the spinel capacity also decreases.

Therefore, the capacity order derived from Figure 7 was expected for Ga, Co (both definitely trivalent), and Li. As for the Ti-doped spinel, XPS experiments have shown that Ti is present as Ti^{4+} . From Table 3, the possibility for Ti^{4+} to form tetrahedral covalent bonds of moderate strength would suggest its occupancy of tetrahedral sites. On the other hand, inverse spinels of the type $\text{M}_x(\text{MTi})_6\text{O}_4$ ($M = \text{Mg}^{2+}$, Co^{2+} , and Zn^{2+})¹⁰ indicate that Ti^{4+} prefers octahedral sites. This is confirmed by literature data on $\text{LiTi}_x\text{Mn}_{2-x}\text{O}_4$, reporting relatively high capacities even for Ti contents as high as 0.8 atom/mol.⁵ Should Ti have occupied tetrahedral sites, one would have recovered a low capacity due to the small amount of Li^+ left in these sites. As for Ni, the capacity order suggests that this element, whose difficult oxidation to Ni^{3+} is known,²⁶ is present in the Ni-doped spinel prepared under N_2 as almost pure Ni^{2+} , in agreement with literature data.^{5,7}

The cycling behavior of the other spinels is shown in Table 7. One may notice for the Cu-doped spinel a stabilized low capacity. Cu^{2+} is a peculiar ion for entering octahedral sites, where it forms strong covalent bonds with a square geometry (dsp^2)¹⁰ and causes a Jahn–Teller effect (it is the only substituent producing this effect). It is interesting to compare the behavior of the Cu-doped spinel with the computer simulation of the energy deviation for Li^+ insertion/extraction of this and other substituted spinels.²⁷ Such a deviation, related to the degree of strain in the crystal structure, was found to be minimized for Cu ($-11 \cdot 10^{-3}$ eV) and quite low (negative) for other elements such as Fe, Co, Ni (of unspecified valence). Conversely, such elements as Ti, Zn, and Ga have positive energies (e.g., $+8.0 \cdot 10^{-3}$ eV for Ga) and, so, are expected to cause structural strains. The Cu-doped spinel has indeed a stabilized capacity (with a relatively low value) and Ni- and Co-doped spinels also perform relatively well, as predicted, but the expected poor performance²⁷ with $M = \text{Ga}$ and Ti is contradicted by our experimental data. At present, we have no details on the calculations of ref 27 and wonder if such important parameters as ionic radii, type of sites occupied, and covalent bond contributions have been taken into account.

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Table 7. Specific Capacities at Selected Cycles and Capacity Losses for the Spinels Not Included in Figure 7

substituent	cycle	specific capacity (mA h/g)										capacity loss for cycles 1–45 (mA h/g cycle)·10 ⁻²	
		1	15	30	45	65	80	100	130	170	200		
Cu		85	86	87	87	88	88	88					
Zn		95	86	84	80								36
Al		96	95	94	93								6.7
B		103	93	86	78								51
Cr		102	100	98	98	96	96	95	95	93	92		8.4
Fe		100	98	97	97	95	95	94					7.6
Ni (air)		102	102	101	100	99							4.4
Co (N ₂)		103	102	101	100	100	99	97	95	93			6.7
Ni–Al		96	92	91	89								15
Ga–Cr		103	100	99	97	97	95						14
Ga–Co		105	105	103	102								5.3

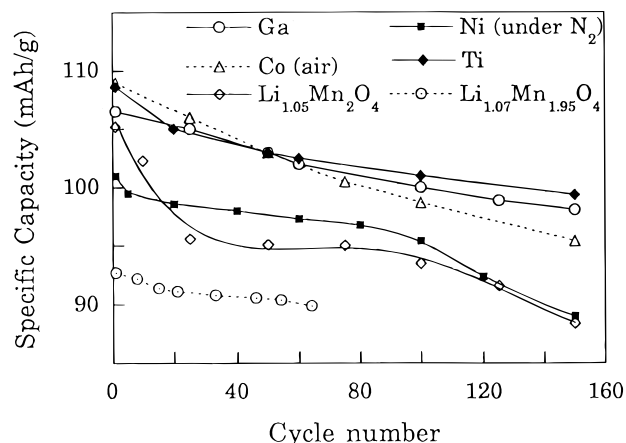
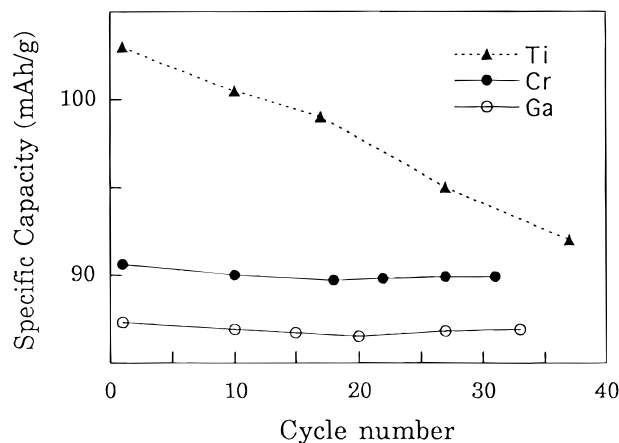
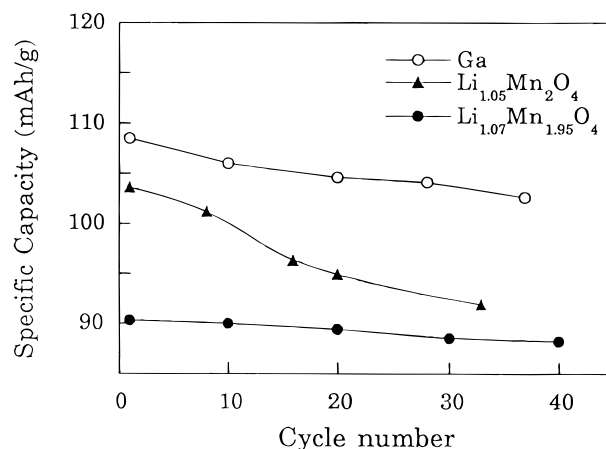
**Figure 7.** Cycling of spinels (indicated in the figure) at 1 mA/cm² (~1 h rate) for charging and discharging, 3.50–4.35 V.

Table 7 affords some other considerations. Al gives low capacities; B causes a fast capacity decay—its low radius (0.27 Å) is likely to strain the structure; Cr and Fe give spinels that cycle well, but a bit less than those with Ga, Co, and Ti. The Co-doped spinel prepared under N₂ has lower capacities than that one made in air (Figure 7), this suggesting that a good fraction of Co²⁺ is present in the former; the Ni-doped spinel in air is, instead, closer to that in N₂, this confirming a large presence of Ni²⁺ in both cases. We have also tried double substitutions with ions occupying both sites. The Ga–Co couple (0.025 atom/mol each) shows a high and relatively stable capacity. The spinel with the Ga–Cr couple is also satisfactory, but the Ni–Al couple shows a relatively low and declining capacity.

Cycling experiments were also carried out at a higher M level with Ti-, Ga-, and Cr-doped spinels (M = 0.1 atom/mol). As shown in Figure 8, the latter two spinels show a reduced and stabilized capacity in comparison with Li_{1.02}Cr_{0.05}Mn_{1.95}O₄ (Table 7) and Li_{1.02}Ga_{0.05}Mn_{1.95}O₄ (Figure 7), respectively. Instead, the Ti-doped spinel shows a relatively high and nonstabilized capacity. As stated before, Ti⁴⁺ substitutes for Mn⁴⁺ in octahedral sites, thus leaving unchanged the Mn³⁺ concentration. So, one would expect a higher capacity with Ti⁴⁺, as indeed found. However, on the same basis, Ti-doped spinels should be insensitive to the Ti⁴⁺ content. But from a comparison of Figures 7 and 8, a higher rate of capacity fading is observed when Ti⁴⁺ increases. The larger Ti⁴⁺ radius vs that of Mn⁴⁺ (0.61 Å or higher [see Table 2] vs 0.53 Å for Mn⁴⁺) is likely responsible for this capacity loss through structural strains. In ref 8, a rapidly decreasing capacity was found for LiTi_{0.2}Mn_{1.8}O₄.

**Figure 8.** Cycling of Li_{1.02}M_{0.1}Mn_{1.90}O₄ spinels (M = Ga, Cr and Ti) at 1 mA/cm².**Figure 9.** High-rate cycling of selected spinels. $I_d = 3$ mA/cm²; $I_c = 1$ mA/cm².

Finally, a cycling test was made at the high rate of 3 mA/cm² (~0.3 h) for Li_{1.05}Mn₂O₄, Li_{1.07}Mn_{1.95}O₄, and Li_{1.02}Ga_{0.05}Mn_{1.95}O₄ (Figure 9). The first spinel has a modest capacity retention, whereas the second has the highest. The Ga-doped spinel has a satisfactory capacity retention and, by far, the highest capacity. This test confirms the trends observed in Figure 7, i.e., Mn³⁺ substitution by either Li⁺ or Ga³⁺ has a positive effect—however, the higher stabilizing effect of Li⁺ is more than compensated by the higher capacity of Ga³⁺.

Conclusions

A number of Mn spinels containing different substituents, M, have been prepared by a solid-state reaction.

For $M = 0.05$ atom/mol, apparently single phases are formed with no appreciable change in the cubic parameter of the original spinel. At higher M levels, e.g., 0.25 atom/mol, some spinels (for instance, those with Ti or Cr) retain the single-phase features, while others (for instance, those with Ga or Co) show some extra peaks suggesting the presence of small amounts of other phases.

The electrochemical tests suggest the following main conclusions.

The stabilization of the spinel capacity afforded by excess Li^+ ($\text{Li}/\text{Mn} \sim 0.58$) causes a capacity decrease to ~ 90 mA h/g.

Some M'' and M''' ions, e.g., Ni, Ga, Co, Fe, and Cr, although showing nonuniform capacity retention, give capacities of ~ 100 mA h/g in long cycling tests at medium-high rates.

Ti^{4+} has good performance at a concentration of 0.05 atom/mol, but at 0.1 atom/mol the capacity is not stabilized. This may be due to a progressive structural strain caused, above a concentration threshold, by an ionic radius larger than that of Mn^{4+} .

Substitution in tetrahedral sites, with formation of spinels of general formula $(\text{Li}_{1-y}\text{M}_y)_t(\text{Li}_{x+y}\text{Mn}_{2-(x+y)})_o\text{O}_{4+z}$ may produce very efficient spinels (e.g., the Ga-doped spinel) through stabilization of the tetrahedral structure.

Even with substitutional levels as low as 0.05 atom/mol, the capacities of the best spinels at practical rates are below 110 mA h/g. Higher capacities reported in the literature are suspicious and may result from the presence of other Li–Mn–O phases.

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