Study of the relationships between the structure of the doped spinels and their electrochemical performance in lithium batteries.

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Abstract. Doping Li-Mn spinels with small amounts of metal ions (Zn, Ni, Co, Cr and Ti in this study) does remarkably affects its structural and electrochemical characteristics.

The parameters *a*, as determined by refinement of the neutron diffraction data, are lower than that of the undoped spinel for all di- and tri-valent dopants and increase with valence (Tab.I). Only for Ti, substituting tetravalent Mn, *a* is larger. With the exception of Zn, which prefers tetrahedral sites and shifts Li in 16d octahedral sites, all dopants have been found in octahedral coordination (16d). The dopants here examined do not favour shifting of Mn into tetrahedral sites as Mn^{2+}, as indicated by the A- and B-site occupancies (Tab.II).

The doped spinels, submitted to extended cycling at the C/2 rate, show capacity fades inversely related to the parameter *a* (Tab.I), i.e. more compact spinels preserve to a larger extent their initial capacities. The high Mn^{4+}/Mn^{3+} ratios do not suggest an important influence of the Jahn-Teller effect.

The capacity losses of the spinels with divalent dopants ($2\text{-}4\cdot10^{-2}$ mAh/g.cycle) are among the lowest thus far reported in the literature. However, Zn- and Mg-doped spinels have low specific capacities (95 and 103 mAh/g, respectively), which do not recommend their use in practical cells. On the other hand, such dopants as Ni, Co and Cr possess at the same time low fade rates ($4\text{-}5\cdot10^{-2}$ mAh/g.cycle) and higher capacities (111 and 109 mAh/g, respectively) (Fig.1).

Table I
Cubic parameters *a*, Mn^{4+}/Mn^{3+} ratios, initial capacities and capacity fading (over 100 cycles) of doped spinels.

Dopant	Dopant Valence	Mn^{4+}/Mn^{3+}	a_{neutr} (A)	Cap. Fading.10^{-2} (mAh/g.cycle)	1st-disch. Cap. (mAh/g)
Zn	2	1.44	8.2105	2	95
Mg	2	"	(8.214)	3	103
Ni	2	"	8.2155	4	111
Co	3	1.29	8.2165	4.5	109
Cr	3	"	8.2170	5	109
Ga	3	"	(8.218)	6	107
None		1.21	8.2211	10	104
Ti	4	1.15	8.2250	13	108
Sb	3	1.29	(8.230)	31	117

Table II

	A-site occupancy for Li (related to the undoped sample)	B-site occupancy for Mn and M (related to the undoped sample)
Undoped	1.00	
Cr	1.00	0.96 0.036
Co	0.97	0.966 0.034
Ni (0.05)	0.98	0.98 0.020
Ni (0.07)	1.00	0.98 0.020
Ti	1.01	-
Zn(0.05)	0.96	0.97
Zn(0.10)	0.92	0.95

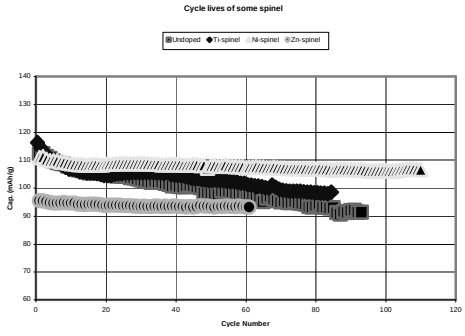

Fig.1