Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Table 1: Structural details for Mn ions in the ground states $Li_{2y}MnSiO_4$ (y = 0.75, 0.5, 0.25 and 0.125): Oxidation state of and distances (in Å) to the neighbours up to 3 Å (see figure S1)

y = 0.75	y = 0.5	y = 0.25	y = 0.125
+2	+3	+3	+4
O 2.0777	O 1.8817	O 1.8454	O 1.8299
O 2.0872	O 1.9512	O 1.9225	O 1.8358
O 2.1040	O 1.9512	O 1.9662	O 1.8400
O 2.1121	O 2.0831	O 1.9710	O 1.9070
O 3.0075	O 2.9521	O 2.2321	O 2.3731
	O 2.9521		O 2.9444
+3	+3	+4	+4
O 1.8353	O 1.9571	O 1.8734	O 1.8398
O 1.9233	O 1.9571	O 1.8794	O 1.8401
O 1.9799	O 2.0049	O 1.9329	O 1.8545
O 1.9823	O 2.0333	O 1.9836	O 1.8871
	O 2.0824	O 2.0980	O 2.2862
	Si 2.7225	O 2.2383	O 2.9624
+3	+3	+4	+3
O 1.8353	O 1.8741	O 1.8269	O 1.8350
O 1.9233	O 1.8871	O 1.8995	O 1.8621
O 1.9799	O 1.8871	O 1.9275	O 1.9104
O 1.9823	O 2.2310	O 1.9872	O 2.1653
	Si 2.7178	O 2.0175	O 2.7864
	O 2.9921	O 2.0409	Li 2.9705
	O 2.9921	Si 2.6279	
+2	+3	+3	+4
O 2.0777	O 1.8757	O 1.8843	O 1.8274
O 2.0872	O 1.9911	O 1.9217	O 1.8400
O 2.1040	O 1.9911	O 1.9853	O 1.8599
O 2.1121	O 2.0032	O 2.1196	O 1.9225
O 3.0075	O 2.0737	O 2.1407	O 2.0486
	Si 2.6998		Si 2.6486
	Li 2.8646		Li 2.7622
	Li 2.8646		O 2.8672

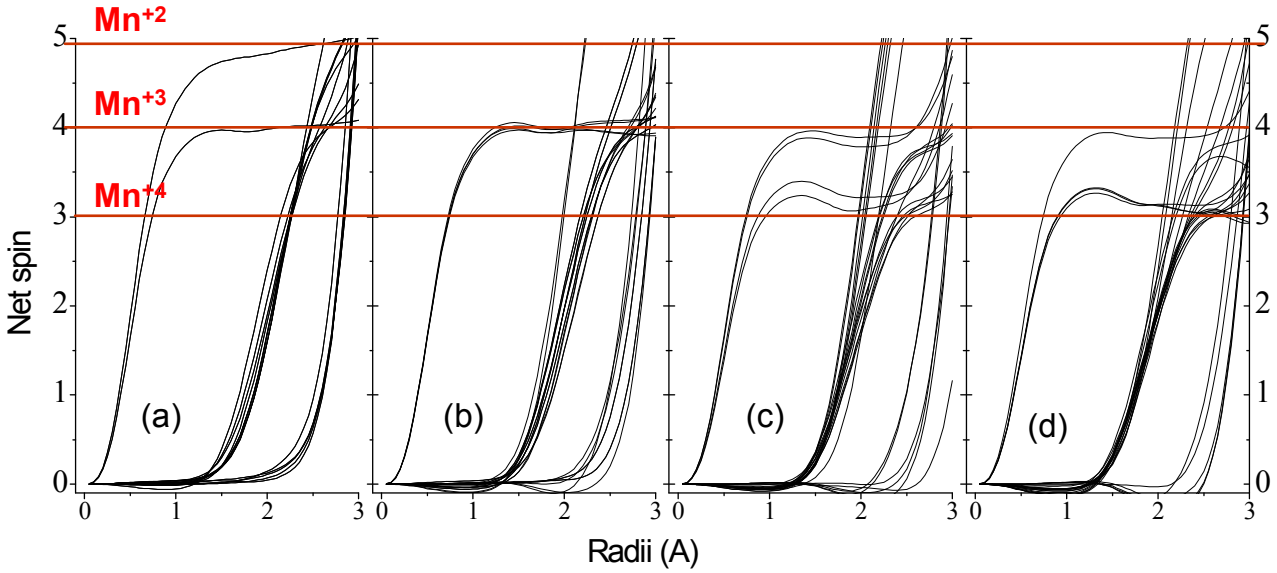

Figure S1.- Integrated net spin as a function of the radius around the ions in the ground states of $Li_{2y}MnSiO_4$ with y = 0.75 (a), 0.5 (b), 0.25 (c) and 0.125 (d)

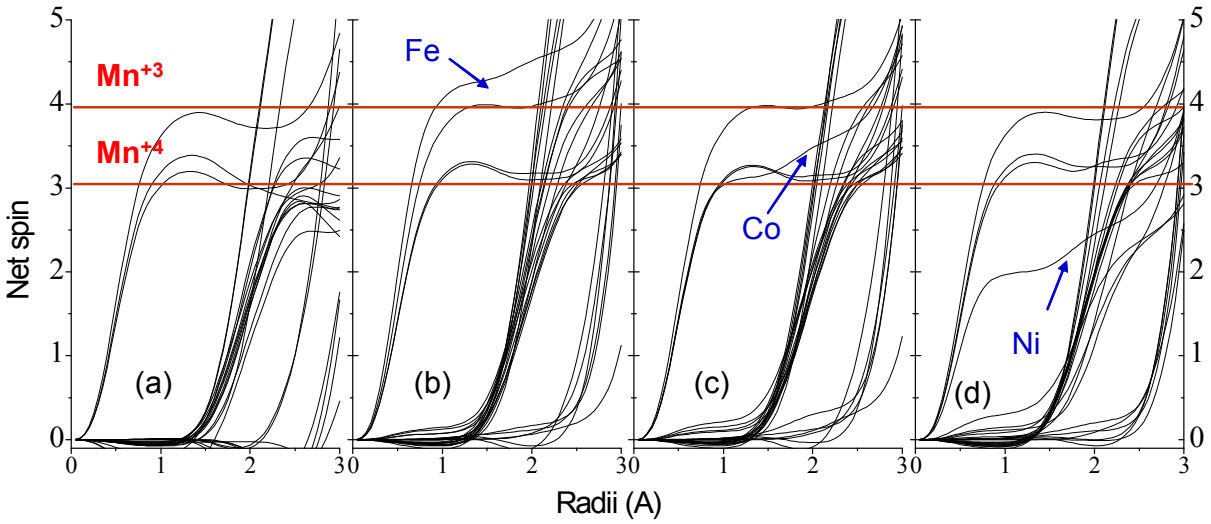

Figure S2.- Integrated net spin as a function of the radius around the ions in the ground states of $Li_{0.5}Mn_{0.75}M_{0.25}SiO_4$ for M = Mg (a) , Fe (b), Co (c) and Ni(d):

Table 2: Structural details for M ions in the ground states $Li_{0.5}Mn_{0.75}M_{0.25}SiO_4$ (M = Mg, Fe, Co, Ni): Approximate oxidation state and distances (in Å) to the neighbours up to 3 Å (see figure S2)

Mg	Fe	Co	Ni
Mn +4 **O 1.8514** **O 1.9173** **O 1.9568** **O 1.9875** **O 2.2737**	**Mn +4** **O 1.8090** **O 1.8559** **O 1.9006** **O 1.9534** **O 1.9595**	**Mn+4** **O 1.8068** **O 1.8512** **O 1.8919** **O 1.9390** **O 1.9670**	**Mn+4** **O 1.8406** **O 1.8451** **O 1.9046** **O 1.9283** **O 1.9791** **Si 2.9598**
Mn +4 **O 1.9001** **O 1.9484** **O 1.9552** **O 1.9639** **O 1.9701** **O 2.1906** **Si 2.6460** **Li 2.9980**	**Mn+4** **O 1.8236** **O 1.8947** **O 1.9137** **O 1.9961** **O 2.0404** **O 2.1248** **Si 2.6398**	**Mn +4** **O 1.8163** **O 1.8946** **O 1.9117** **O 1.9858** **O 2.0369** **O 2.0987** **Si 2.6195**	**Mn+3** **O 1.8751** **O 1.9196** **O 1.9803** **O 2.0269** **O 2.1014**
Mn +4 **O 1.8374** **O 1.8961** **O 1.9058** **O 1.9976** **O 2.0103** **O 2.0271** **Si 2.5994**	**Mn+3** **O 1.8937** **O 1.9620** **O 1.9732** **O 2.1086** **O 2.1492**	**Mn+3** **O 1.8889** **O 1.9398** **O 1.9578** **O 2.1351** **O 2.1701**	**Mn +4** **O 1.8371** **O 1.8513** **O 1.8732** **O 1.9747** **O 2.0640**
Mg+2 **O 1.9505** **O 2.0360** **O 2.0386** **O 2.0518** **O 2.1680**	**Fe+3** **O 1.9060** **O 1.9089** **O 1.9376** **O 2.0205** **O 2.0997** **Li 2.9017**	**Co +3** **O 1.8809** **O 1.9096** **O 1.9167** **O 1.9870** **O 2.1352** **Li 2.9089** **Si 2.9706** **O 2.9921**	**Ni +2** **O 1.7953** **O 1.8926** **O 1.9596** **O 1.9597** **O 2.1440** **Li 2.8808**

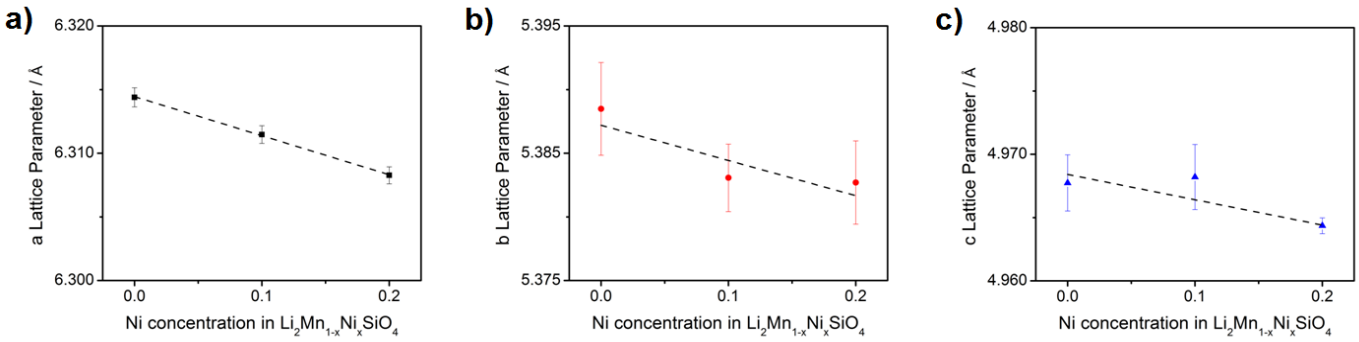

Figure S3. Lattice Parameter variation of Ni doped $Li_2Mn_{1-x}Ni_xSiO_4$ showing decrease in all three parameters.

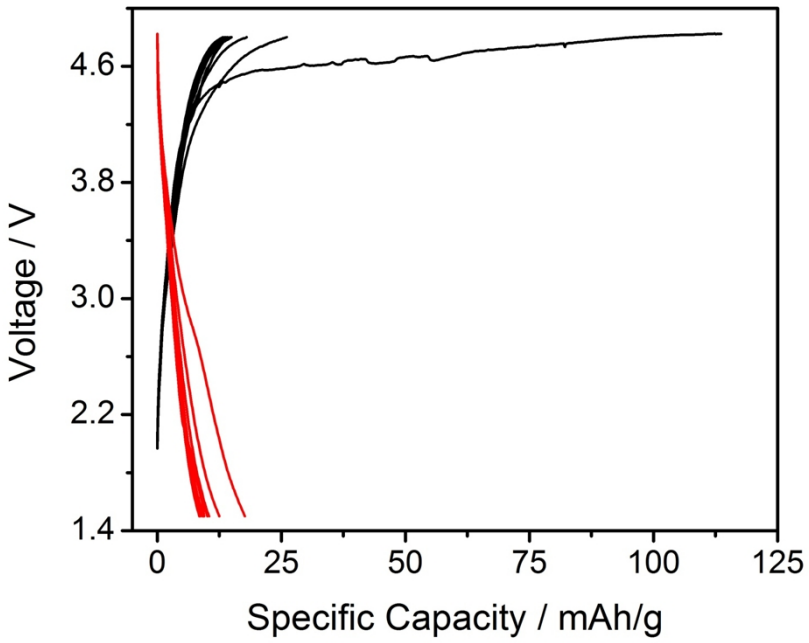

Figure S4. Cycling of as prepared Li_2MnSiO_4 Voltage window of 4.8 – 1.5 V was used at a C/20 rate.

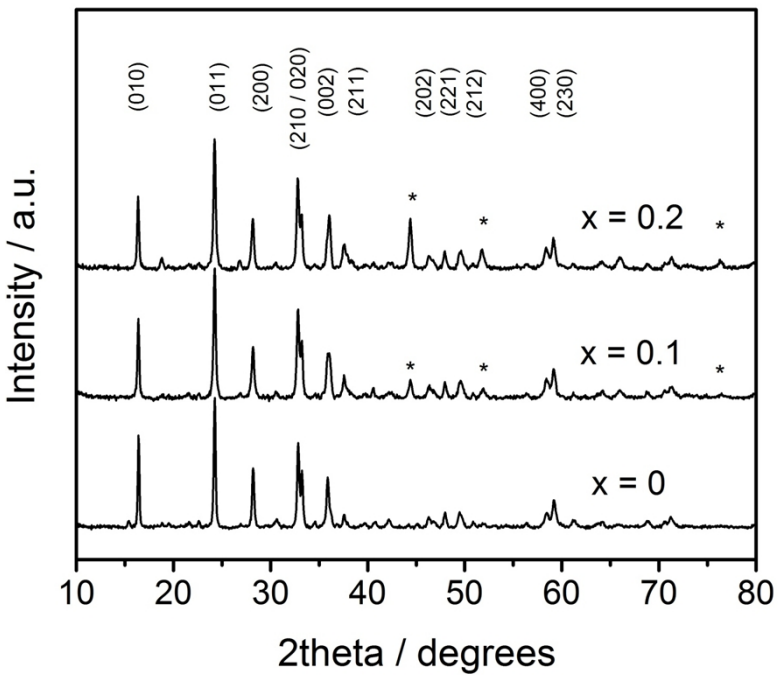

Figure S5. Powder X-ray diffraction pattens of $Li_2Mn_{1-x}Ni_xSiO_4$ samples after the carbon coating process. Asterisk denotes Bragg maxima assignable to metallic Ni.

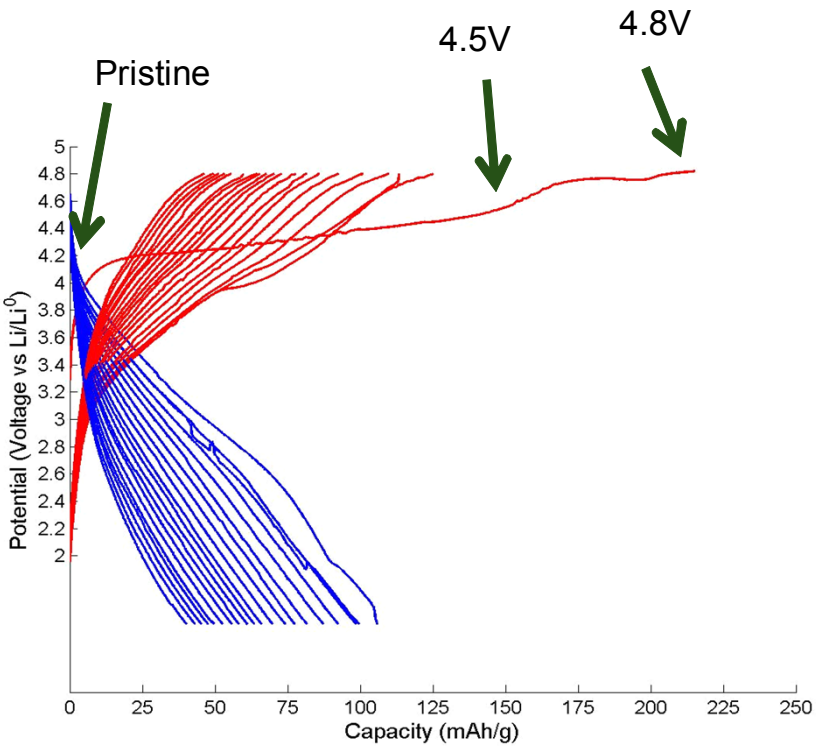

Figure S6. Cycling of a carbon coated $Li_2Mn_{1-x}Ni_xSiO_4$ // Li cell. *Ex situ* XPS were collected at points A, B and C during the first charge.