Details of Methodology

All the calculations in this work were performed using full-potential linear augmented plane wave (FP-LAPW) method within the framework of density functional theory (DFT),[21] as implemented in the WIEN2K code.[21] For the assessment of structural/electrochemical properties, including structural parameters, theoretical charge/discharge reaction voltage (TRV), magnetic moment (μ_B) and density of states (DOS), the calculations were carried out using Perdew–Burke–Ernzerh generalized gradient approximation (PBE-GGA)[23] local spin density approximation (LSDA), generalized gradient and local density approximations plus an on-site Coulomb self-interaction correction potential (GGA+U^{SIC} and LDA+U^{SIC}, respectively). Two versions of calculations spin-polarized i) ferromagnetic (FM) and ii) anti-ferromagnetic (AFM), were employed. Inside the non-overlapping spheres of muffin tin radius (R_{MT}) around each atom, linear combination of radial solution of the Schrödinger equation times the spherical harmonic are used and the plane wave basis set is used in the interstitial region. R_{MT} values 2.00, 1.90, 1.86, 1.75 and 1.78 a.u. were used for Mn, Fe, Co, Ni and Li, respectively, and 1.52 a.u. for Si and O atoms. To expand the wave functions in the interstitial region a plane wave cut-off value of K_{max} .R_{MT} =7.0 was used. The Fourier-expanded charge density was truncated at G_{max}=12 $(Ryd)^{1/2}$. The maximum value of the angular momentum (l_{max}) was set equal to 10 for the wave function expansion inside the atomic spheres. Convergence of the self-consistent iterations was performed within 0.0001 Ry.

The electron and spin configurations are software defaults and are Mn_{up}: [Ar] $3d^5(5\uparrow, 0\downarrow)$ $4s^2(1\uparrow, 1\downarrow)$, Mn_{non}: [Ar] $3d^5(2.5\uparrow, 2.5\downarrow)$ $4s^2(1\uparrow, 1\downarrow)$, Fe_{up}: [Ar] $3d^{6.5}(4.5\uparrow, 2\downarrow)$ $4s^{1.5}(1\uparrow, 0.5\downarrow)$, Fe_{non}: [Ar] $3d^7(3.5\uparrow, 3.5\downarrow)$ $4s^1(0.5\uparrow, 0.5\downarrow)$, Co_{up}: [Ar] $3d^7(5\uparrow, 2\downarrow)$ $4s^2(1\uparrow, 1\downarrow)$, Co_{non}: [Ar] $3d^8(4\uparrow, 4\downarrow)$ $4s^2(0.5\uparrow, 0.5\downarrow)$, Ni_{up}: [Ar] $3d^8(5\uparrow, 3\downarrow)$ $4s^2(1\uparrow, 1\downarrow)$ and Ni_{non}: [Ar] $3d^8(4\uparrow, 4\downarrow)$ $4s^2(1\uparrow, 1\downarrow)$ for up and no spin polarization for Mn, Fe, Co and Ni atoms, respectively. For FM calculations spin up was used as majority direction and for AFM calculations no-spin was used. No spin polarization is considered for the other non-magnetic atoms in the unit cell. Atomic configuration for these atoms are Li: [He] $2s^1$, Si: [Ne] $3s^2$ $3p^2$ and O: [He] $2s^2$ $2p^4$.

The structure with *Pmn2₁* space group suggested by Nytén et al.[24] for Li_2FeSiO_4 was used as the initial structure for all DFT calculations. In order to perform the $Li_2M_{0.5}N_{0.5}SiO_4$ assessment, one unit cell of *Pmn2₁* structure with one atom of M and one atom of N was assumed. Fig. S1 illustrates considered $Li_2Mn_{0.5}Ni_{0.5}SiO_4$ structure as an example. In order to obtain total energies, magnetic state and DOS (so band-gaps), integrals were calculated over the Brillouin zone with k-points based on 4×5×5 Monkhorst–Pack (MP) mesh. This grade contains 18 and 50 k-points in the irreducible Brillouin zone for *Pmn2₁* space group (Li_2MSiO_4) and *P₁* space group (U^{SIC} calculations for Li_2MSiO_4 and all calculations for $LiMSiO_4$, $Li_2M_{0.5}N_{0.5}SiO_4$ and $LiM_{0.5}N_{0.5}SiO_4$), respectively.

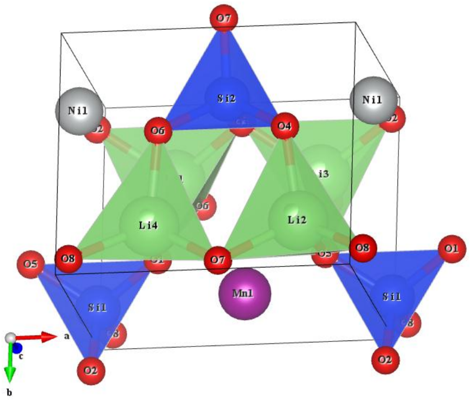

Fig. S1 considered $Li_2Mn_{0.5}Ni_{0.5}SiO_4$ structure with Pmn21 space group.

Relaxation process was carried out in three modes, including geometry minimization of the atomic positions according to inter-atomic forces (mini. positions), optimization volume with constant a:b:c ratio and with variable a, b, c (for orthorhombic). Regarding mini. positions calculations, force set at 0.001 $Ry.au^{-1}$. Delithiated structure configuration is assumed to be the most stable one.

For more comprehensive results and to calculate more accurate electrical properties, PBE-GGA and LDA plus an on-site Coulomb self-interaction correction potential (U^{SIC}) were applied, hereinafter called GGA+U^{SIC} and LDA+U^{SIC}, respectively. The U^{SIC} value was considered to be equal to 6 eV for Mn, Co and Ni and 5 eV for Fe atom (based on Arroyo-deDompablo et al.[1] and Wu et al.[2] works). To obtain relaxed atomic positions and crystal parameters, U^{SIC} was not applied since this parameter does not lead to significant changes in the structural properties.

To recognize segregation of $LiM_{0.5}N_{0.5}SiO_4$ in lithiated and delithiated conditions reaction (S1) and (S2) are considered, respectively.

$$2(Li_2M_{0.5}N_{0.5}SiO_4) \rightarrow Li_2MSiO_4 + Li_2NSiO_4 \qquad (S1)$$

$$2(LiM_{0.5}N_{0.5}SiO_4) \rightarrow LiMSiO_4 + LiNSiO_4 \qquad (S2)$$

An important electrochemical character that can be evaluated directly from the difference in total energies before and after extraction of lithium is theoretical lithiation/delithiation reaction voltage (hereinafter named TRV). This parameter is calculated in this study from charge reaction (1), and is obtained by equation (2):

$$Li_2M_{0.5}N_{0.5}SiO_4 \dashrightarrow LiM_{0.5}N_{0.5}SiO_4 + Li \qquad (1)$$

$$TRV = E_{LiM_{0.5}N_{0.5}SiO_4} + E_{Li} - E_{Li_2M_{0.5}N_{0.5}SiO_4} \qquad (2)$$

Where $E_{Li_2M_{0.5}N_{0.5}SiO_4}$ and $E_{LiM_{0.5}N_{0.5}SiO_4}$ are the calculated total energies (eV) of one unit formula for lithiated and delithiated structures, respectively. E_{Li} is the calculated total energy for one atom of lithium metal in the bcc lattice. To determine E_{Li}, the relaxation process was carried out with optimization volume (k-points = 7×7×7 and $E_{conv.}$= 0.0001 Ry), then the total energy (E_{Li}) was calculated based on 3094 k-points in the irreducible Brillouin zone (50×50×50 grid), by setting energy convergence at E=0.00001 Ry. For Li_2FeSiO_4, all data are taken from Ref. 19.

Structural Parameters and Stability

Table S1 shows structural parameters and cell volumes of $Li_2M_{0.5}N_{0.5}SiO_4$ materials calculated via GGA and LSDA methods. This table is sorted with respect to the calculated total energies, the most stable material being that with M, N=Ni. In order to state the structure stability after the extraction of one Li-ion per formula unit, changes in structure after delithiation are given. This table shows that all of these materials are structurally stable after delithiation. This could be expected because of the strong silicate framework in *Pmn2₁* space group (s.g.).

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[1] M. E. Arroyo-deDompablo, M. Armand, J. M. Tarascon, U. Amador, Electrochem. Commun. **2006**, 8, 1292–1298.

[2] S. Q. Wu, Z. Z. Zhu, Y. Yang, Z. F. Hou, Comput. Mat. Sci. **2009**, 44, 1243–1251.

Table S1. Calculated structural parameters, unit cell volume, and changes in unit cell volume after delithiation, obtained via GGA and LSDA methods.

	method	a (A)	b (A)	c (A)	Ω (A^3)	$(\Omega_2-\Omega_1)/\Omega_1$(%)
Mn	PBE-GGA	6.2519	5.2905	4.929	163.0308	0.9981
	LSDA	6.1781	5.2281	4.8708	157.3248	-1
Mn-Fe	PBE-GGA	6.1362	5.324	4.9852	162.8638	-1.4112
	LSDA	6.0742	5.2702	4.9349	157.9779	1.6379
Fe	PBE-GGA	6.2208	5.2905	4.9788	163.8583	0.9709
	LSDA	6.2408	5.3076	4.9949	165.4492	-1
Mn-Co	PBE-GGA	6.1661	5.3076	4.9949	163.4671	0.0289
	LSDA	6.1083	5.2579	4.958	159.232	-0.3065
Fe-Co	PBE-GGA	6.1944	5.2681	4.9626	161.9431	-0.5849
	LSDA	6.1271	5.1849	4.8793	155.0086	-0.4048
Mn-Ni	PBE-GGA	6.2212	5.2909	4.9641	163.3969	-2.5508
	LSDA	6.1371	5.2194	4.897	156.8609	1.0021
Co	PBE-GGA	6.1882	5.2628	4.9527	161.2958	1.8098
	LSDA	6.1257	5.2096	4.9027	156.4569	0.3
Fe-Ni	PBE-GGA	6.2005	5.2733	4.9626	162.2655	-0.7812
	LSDA	6.1579	5.2109	4.9039	157.3571	-0.2015
Co-Ni	PBE-GGA	6.1802	5.2561	4.9118	159.5536	2.3223
	LSDA	6.1518	5.2057	4.899	156.8856	-0.7027
Ni	PBE-GGA	6.1432	5.2508	4.9414	159.3941	0.1938
	LSDA	6.0916	5.2067	4.8999	155.4092	2.0000

Segregation Energies

Table S2 shows reaction free energies, Δ_rG, for reactions (S1) and (S2). Negative sign means phase separation. Here it is assumed that all the orthosilicates Li_2MSiO_4 (M= Mn, Fe, Co and Ni) would be accessible. However, Mn, Fe (see e.g. Ref. 5 and references therein) and Co[3] lithium orthosilicate materials were synthesized, but to our knowledge there is not yet any experimental evidence of Li_2NiSiO_4. Table S2 does not lead to unique conclusions about phase separation due to the sign scattering obtained from the different calculation methods, except of Mn-Co compound for which all calculations predict the negative sign for reaction (S1). On the other hand, LSDA-FM calculations predict phase separation for all mixed compounds. It must also be considered that the absolute values of the obtained energies are relatively low.

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[3] A. R. Armstrong, C. Lyness, M. Ménétrier, P. G. Bruce, Chem. Mater. **2010**, 22, 1892–1900.

Table S2. Calculated reaction energies (Δ_rG, kJ/mol) for equation (S1) and (S2) (lithiated and delithiated, respectively) obtained by different computational methods.

material	condition	GGA-FM	GGA-AFM	LSDA-FM	LSDA-AFM	GGA+U	LSDA+U
Fe-Mn	lithiated	-1.28	-0.03	-1.31	1.49	9.77	18.03
	delithiated	2.11	4.39	0.46	3.13	13.00	16.54
Mn-Co	lithiated	-3.95	-1.31	-24.17	-21.53	-6.06	-20.09
	delithiated	2.35	3.55	-22.52	-26.00	0.58	-17.86
Fe-Co	lithiated	0.81	1.52	-22.42	-22.41	-1.74	-7.80
	delithiated	0.45	2.64	-21.52	-24.10	12.71	-7.38
Mn-Ni	lithiated	-3.40	2.08	-1.30	4.22	-8.11	-3.12
	delithiated	4.16	4.90	4.22	7.42	-2.53	4.11
Fe-Ni	lithiated	2.59	4.02	-31.67	-28.36	6.94	-20.08
	delithiated	2.05	2.64	-30.78	-31.15	3.11	-10.89
Co-Ni	lithiated	2.19	1.69	-27.29	-27.23	1.56	-28.38
	delithiated	1.15	1.02	-27.87	-27.14	1.59	-27.00

A possible presentation data in order to estimation of other compounds

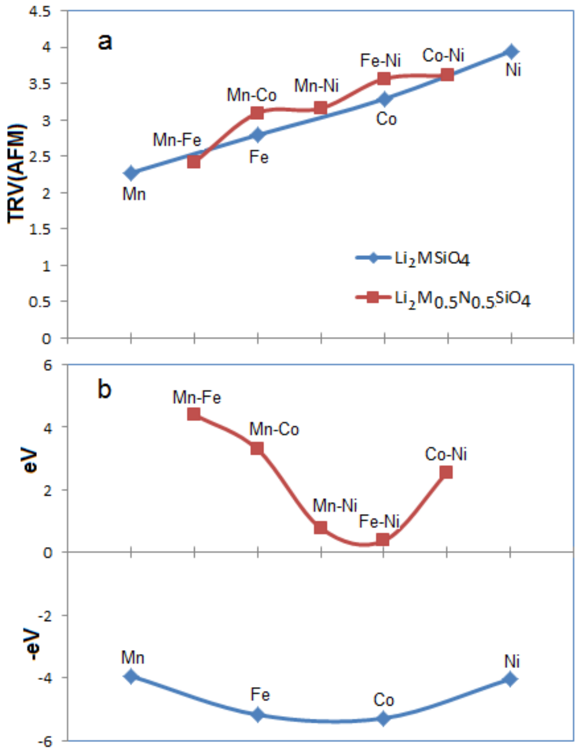

Fig. S2. TRV-AFM (a), and BG summation of lithiated and delithiated (b) for Li_2MSiO_4 and $Li_2M_{0.5}N_{0.5}SiO_4$ materials, sorted by electron number in *3d* orbital.

According to Fig. S2, TRV-AFMs of $Li_2M_{0.5}N_{0.5}SiO_4$ as well as Li_2MSiO_4 materials increase almost linearly by electron number in *3d* orbital (or/and molecular mass). On the other hand, summation of band gap in lithiated and delithiated states for $Li_2M_{0.5}N_{0.5}SiO_4$ and Li_2MSiO_4 materials act in opposite way. The highest (Co) and the lowest (Fe-Ni) band gaps are located at the same place. This figure could be worthy to estimate properties of other ratios between translation metals.