New insights into the electrochemical performance of Li$_2$MnSiO$_4$: effect of cationic substitutions†

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The performance of the Li$_2$MnSiO$_4$ cathode material is hindered by voltage decay and capacity fading caused by structural instability. To rationalize the origin of such structural instability, we have investigated a total of 142 Li$_2$Mn$_y$SiO$_4$ configurations at $y = 0.125, 0.25, 0.333, 0.375, 0.417, 0.5, 0.625, 0.666, 0.75$ and $0.875$ by density functional theory methods. It is found that the most stable Li$_2$Mn$_y$SiO$_4$ configurations with $y = 0.5$ consist of Mn$^{4+}$ and Mn$^{3+}$ in octahedral or five-fold coordination. This induces a crystal deformation, loss of the orthogonal symmetry, and a notorious volume decrease ($7\%$ for LiMnSiO$_4$ and $14\%$ for Li$_0.5$MnSiO$_4$). The effect of Mn substitution on the crystal structure of the delithiated silicates Li$_x$Mn$_{0.75}$Mg$_{0.25}$SiO$_4$ is computationally investigated for $M = Mg, Fe, Co$ and $Ni$. The most stable configurations for Mg, Fe and Co substitutes possess Mn$^{3+}$ in octahedral coordination, sharing edges with the adjacent Si and Mn polyhedra.

DFT results suggest that among the studied substituents, only Ni could help to maintain the structural integrity of the delithiated samples. Experimentally, Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$ samples with $x = 0, 0.1$ and $0.2$ were synthesized and electrochemically tested.

Introduction

Lithium-ion batteries are essential in portable electronics and are becoming a competitive technology for larger-scale application in transportation and grid stabilization of renewable sources (i.e. wind and solar). However, to support the increasing demand for energy and power, urgent improvements are needed; one of the current strategies is to increase the specific capacity. In this sense, lithium transition metal (Li$_2$MSiO$_4$, $M = Fe, Mn, Co, Ni$) silicate materials have been presented as promising cathode materials for lithium ion batteries.1-4 The key advantage of these silicates is their theoretical capability to reversibly de-intercalate two lithium equivalents from the structure, giving a very high theoretical capacity of about 333 mA h g$^{-1}$. The most promising candidates are the Li$_2$FeSiO$_4$ and Li$_2$MnSiO$_4$. With Fe redox potentials at 3.1 V (Fe$^{3+}$/Fe$^{2+}$) and 4.7 V (Fe$^{4+}$/Fe$^{3+}$) and both Mn redox potentials (Mn$^{3+}$/Mn$^{4+}$ and Mn$^{3+}$/Mn$^{4+}$) mixed at 4.0 V, these materials have electrochemical processes within the stability of organic electrolytes, this is, up to ca. 4.8 V against a Li$^+$/Li electrode.5

The crystal structure of Li$_2$MSiO$_4$ consists of a distorted hexagonal packing of oxygen ions with half of the tetrahedral sites occupied by Li, $M$ and Si.6 A large number of Li$_2$MSiO$_4$ polymorphs are possible by assuming a different pattern of occupancy of the tetrahedral voids in the distorted hexagonally packed anion framework. Fig. 1a shows the crystal structure of the $Pmn2_1$ polymorph which has been determined as the most stable polymorph for $M = Fe$ and Mn.5-7 The crystal cell consists of only corner-sharing tetrahedra, all pointing toward the same orientation along the $c$ axis. It is a 2-D structure built up from infinite corrugated layers of composition [SiMO$_4$]$_n$ lying on the $ac$-plane and linked along the $b$-axis by Li$_2$O tetrahedra.

For the two electron process, Li$_2$MnSiO$_4$ provides more advantages than Li$_2$FeSiO$_4$. Since in Li$_2$MnSiO$_4$ the voltage jump between the first and second lithium extraction does not proceed through the large jump that Li$_2$FeSiO$_4$ encounters,4,5 Li$_2$MnSiO$_4$ offers the possibility of the second lithium extraction at a lower cell voltage. A recent review discusses the preparation techniques, structural issues, conductivity enhancement and complex morphologies of reported Li$_2$MnSiO$_4$ electrode materials.8 Unfortunately many experimental efforts have failed to achieve a good electrochemical performance even in the one electron process, due to the structural instability of Li$_2$MnSiO$_4$ upon delithiation.7,10-15 Calculations at the Density Functional Theory level (DFT) support the tendency of the Li$_2$MnSiO$_4$ structure to collapse upon delithiation of more than one Li ion.5,11 Attempts have also been made to stabilize the crystal structure of delithiated Li$_2$MnSiO$_4$ by partial Fe substitution for Mn, as suggested by DFT...
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The electrochemical properties of Li2MnSiO4. Aiming to improve understanding is important to route the experimental electrode materials upon delithiation. DFT results suggest that the structural distortion in the possible modifications of the crystal lattice suggests that Mn3+/Mn4+ reversibility and cycling stability.29 To the best of our knowledge, the electrochemistry of other substituted Li2Mn1−xMxSiO4 electrode materials has not been reported.

Currently, a rational explanation of the structural instability of the delithiated Li2MnSiO4 phases is still lacking. This understanding is important to route the experimental efforts in the possible modifications that could lead to improved electrochemical properties. In the present work, we investigate and rationalize the origin of the crystal distortion in Li2MnSiO4 silicates upon delithiation. DFT results suggest that the structural instability is related to the trend of Mn3+/Mn4+ ions to adopt an octahedral coordination. DFT is a powerful tool to anticipate the effect of cationic substitutions on the electrochemical properties of Li2MnSiO4. Aiming to improve the electrode characteristics of Li2MnSiO4, we have explored the role of Mg, Fe, Co and Ni as possible substitutes for Mn (Li2Mn0.75M0.25SiO4). We will show that Mn substitution by Ni might help to prevent the structural collapse. A novel experimental investigation of the Li2Mn1−xNiSiO4 electrode materials is finally presented.

Methodology

Computational

The total energies of Li2MSiO4 were calculated using the ab initio methods implemented in the Vienna Ab initio Simulation Package (VASP).26-28 The Projector Augmented Wave (PAW) potential set29 was used with the exchange and correlation energies approximated in the generalized gradient approximation with the Hubbard parameter correction (GGA + U) following the rotationally invariant form.26,28 An effective U value of 4 eV (J = 1 eV) was used for the d states of TM ions. The energy cut off for the plane wave basis set was kept fixed at a constant value of 600 eV throughout the calculations. The integration in the Brillouin zone is done on an appropriate set of k-points determined by the Monkhorst-Pack scheme. A convergence of the total energy close to 5 meV per formula unit is achieved with such parameters. The structures were fully relaxed (cell parameters, volume cells and atomic positions).

The initial atomic positions for Li2MnSiO4 were taken from the proposed orthorhombic structure for Li2MnSiO4 (space group Pmn21) which is the most stable one. For the intermediate phases, Li2MnSiO4 lithium-vacancy arrangements have been created using the CASM (Cluster-Assisted Statistical Mechanics) software package.21,22 We have computed a total of 142 configurations in the Pmn21 host, using supercells of up to 6 formula units (Li12Mn8Si6O24). The investigated Li2MnSiO4 configurations have y values of 0.125, 0.25, 0.333, 0.375, 0.417, 0.5, 0.625, 0.75 and 0.875. For the half delithiated phase (y = 0.5), we have tested up to 35 different lithium-vacancy arrangements.

Substituted Li2Mn0.75M0.25SiO4 (M = Mg, Fe, Co, and Ni) silicates have been investigated for y = 0.75 and y = 0.25 with a unit cell containing 4 formula units. The lithium-vacancy ordering corresponds to the detected ground state for the pure Mn silicate. The calculations have been initialized incorporating the lithium vacancies in the pristine Li2MnSiO4 crystal structure (orthogonal Pmn21 symmetry). Any possible ordering of Mn and M ions within this cell was also computed. Cell volume and shape together with atomic positions have been fully relaxed.

Experimental

Among the various synthesis routes utilized to prepare Li2MnSiO4, the solvothermal synthesis has produced the materials with the best electrochemical characteristics. In this work, we have prepared Li2Mn1−xNiSiO4 (x = 0, 0.1, 0.2) compounds utilizing the solvothermal method used by Aravindan et al.21 NiCl2·6H2O and MnCl2·4H2O (Sigma Aldrich, 99.99%) were used in proportions to produce Li2Mn1−xNiSiO4 (x = 0, 0.1, 0.2). First, 0.386 g (0.0092 mol) of LiOH·H2O was added to 5 mL of deionized water. Then, 0.138 g (0.0023 mol) of metal chlorides were dissolved in 10 mL of ethylene glycol by stirring. The two solutions were then combined and further stirred for one hour before placing in a 23 mL Parr 4749 acid digestion vessel. The vessel was heated at 150 °C for 48 hours and the product was filtered and dried at 60 °C overnight. For carbon coating, the as-synthesized material was mixed with 30 wt% sucrose (Sigma Aldrich > 99.5%) and pelleted. The pellet was then heated at 700 °C in an Ar atmosphere for 10 hours.
Results and discussion

(A) Formation energies and ground states in Li$_2$MnSiO$_4$

We have evaluated the stability of Li$_{2y}$MnSiO$_4$ ($0 < y < 1$) phases according to the reaction:

$$y\text{Li}_2\text{MnSiO}_4 + (1-y)\text{MnSiO}_4 \rightarrow \text{Li}_{2y}\text{MnSiO}_4 \tag{1}$$

Fig. 2 shows the formation energies of the computed 142 different lithium vacancy arrangements. The formation energy of Li$_{2y}$MnSiO$_4$ is defined as:

$$\Delta_y E = E - yE_{\text{Li}_2\text{MnSiO}_4} - (1-y)E_{\text{MnSiO}_4} \tag{2}$$

where $E$ is the total energy of the Li$_{2y}$MnSiO$_4$ configuration per formula unit, $E_{\text{Li}_2\text{MnSiO}_4}$ is the totally energy of the delithiated phase and $E_{\text{MnSiO}_4}$ is the energy of the delithiated $Pmn2_1$ MnSiO$_4$ host. The convex hull (line connecting the lowest phases in the formation energy versus composition curve) is displayed in Fig. 2. While for Li$_2$FeSiO$_4$ the convex hull is governed by a unique and pronounced ground state at $y = 0.5$ (see ref. 9), the convex hull of Li$_{2y}$MnSiO$_4$ presents ground states at $y = 0.125$, $y = 0.5$ and $y = 0.25$.

The crystal structures of the most stable Li$_{2y}$MnSiO$_4$ configurations at $y = 0.75$, $y = 0.5$ and $y = 0.25$ are shown in Fig. 1. The Mn–O bond distances are listed in the ESI.† The oxidation state around each Mn ion was approximated by integrating the unpaired electron density within a sphere of radius 3.0 Å, but excluding the density coming from the oxygen ions (see Fig. 1 in the ESI†). The most stable configuration at $y = 0.75$ consists of half Mn$^{3+}$ and half Mn$^{4+}$, all of them retaining the tetrahedral coordination of the pristine material. At this level of delithiation, minor structural distortions are predicted with a cell volume variation of only 0.2%, though with a small deviation from the orthogonal symmetry ($\gamma = 93^\circ$).

From the 35 explored arrangements at $y = 0.5$, the most stable structure (displayed in Fig. 1c) consists of a supercell containing four Li$_2$MnSiO$_4$ formula units, with two of the four Mn$^{3+}$ ions presenting a five-fold coordination, and the other two a six-fold coordination with four short distances and two long ones (2.9 Å). When analyzing the observed distortion in depth, it turns out that the coordination change in manganese is accompanied by significant changes in O–Mn–O angles. Distortions of Li$_{2y}$MnSiO$_4$ materials dominated by changes in O–Mn–O angles have been reported by other authors.5,25 The predicted cell volume contraction relative to Li$_2$MnSiO$_4$ is 6.8% and there is a deviation from the orthogonal symmetry ($\gamma = 87^\circ$). Note that this volume variation is greater than that predicted previously 0.37% in ref. 5 and 2.0% in ref. 13 where only the three possible configurations in the unit cell (two formula units) were considered. In the present work, a deeper analysis of LiMnSiO$_4$ configurations allows the prediction of crystal modifications consistent with the poor cycling retention of Li$_2$MnSiO$_4$ even for the one electron process.

In the ground state at $y = 0.25$ [Li$_{0.5}$Mn$_{0.5}$$^{3+}$Mn$_{0.5}$$^{4+}$SiO$_4$] the Mn$^{3+}$ and Mn$^{4+}$ ions are in quite distorted five-fold or six-fold coordination (Fig. 1d). The cell volume diminished 13.7% respective to the pristine material. In addition, the cell distorts losing the orthogonal shape ($\alpha = 85^\circ$ $\beta = 90^\circ$ $\gamma = 75^\circ$) and edge sharing polyhedra are distinguished. Analysis of other low energy Li$_{2y}$MnSiO$_4$ configurations confirms that at low Li contents ($y \leq 0.5$) the Mn ions do not retain a tetrahedral coordination.

![Fig. 2](image-url)
Due to the large crystal distortions in delithiated materials it is not possible to perform a cluster expansion of the calculated formation energies and using it in Monte Carlo methods to simulate the voltage-composition curve of Li₂MnSiO₄ as was done for Li₂FeSiO₄ and layered-LiMO₃ (M = Co, Ni) materials. Yet, a scratch of the voltage profile can be extracted from the calculated total energy of the ground states lying on the convex hull. Fig. 3 shows the sketch of the voltage–capacity curve of Li₂MnSiO₄ at 0 K, compared with the experimental profile collected in this work (experimental 1) and with the profile taken from Muraliganth et al. As discussed below our experimental setting results in a lower specific capacity than that obtained in ref. 24. In the calculated profile, for the specific capacity below 300 A h kg⁻¹, the voltage steps between two consecutive single phase regions are small (around 0.15 V). Above 0 K, entropy effects would smooth the voltage-composition profile, resulting in a sloping voltage curve with no detectable ordered phases in agreement with experimental observations. At ca. 300 A h kg⁻¹, a greater voltage jump of 0.55 V is predicted, which corresponds to the de-insertion of 1.75 Li ions (formation of Li₁.₅MnSiO₄ with y = 0.125). The calculated average voltage for this last voltage plateau is 4.9 V. This voltage jump seems consistent with the experimental curve, even though the maximum theoretical capacity (333 A h kg⁻¹) has not been reached in practice.

Comparison of the electrode characteristics of Li₂FeSiO₄ and Li₂MnSiO₄ showed that both materials are stable in the 2D-Pmmn²¹ polymorph, though various 2D and 3D polymorphs compete in energetic stability, all of them have very similar de-intercalation voltages. For Li₂FeSiO₄, due to the high stabilization of the d⁵ configuration, at half delithiation a unique very stable configuration lies in the convex hull. This causes a pronounced voltage step of 2 V in the electrochemical curve at y = 0.5. In all the investigated 2D and 3D Li₂FeSiO₄ (0 < y < 1) configurations the crystal cell maintains the orthorhombic shape and Fe cations appear in tetrahedral coordination. Upon delithiation the system is driven by the need for minimizing electrostatic repulsions, which are ameliorated in the 3D polymorphs. For this reason, Li₂FeSiO₄ suffers from a phase transformation upon delithiation. Unfortunately, delithiation of the 3D structure is accompanied by a large volume variation (around 20%), which precludes the reversible intercalation of the two Li ions.

Unlike Li₂FeSiO₄, the fully de-inserted MnSiO₄ is more stable in the 2D structure than in a 3D structure. Recent data from Lee et al. support this result, though these authors predict an unreasonable voltage-composition curve with the deinsertion voltage of the first lithium from Li₁MnSiO₄ above that of the second lithium ion. In the present work from the analysis of the most stable configurations, we can conclude that lithium de-intercalation from Li₂MnSiO₄ irremediably causes a local distortion of the Mn polyhedra, severe crystal structure deformation, and large volume contraction. None of these features are found in delithiated 2D or 3D-Li₂FeSiO₄ (0 < y < 1) configurations.

Differences between Li₂FeSiO₄ and Li₂MnSiO₄ are not surprising; for isostructural compounds, the electronic configuration of the transition metal ion plays a role in the phase stability upon lithium deinsertion. Table 1 lists the crystal field stabilization energies in the 6-fold, 5-fold and 4-fold coordination for Mn ions in different oxidation states. The closed shell Mn⁵⁺ is equally stable in any coordination. Mn⁷⁺ is more stable in the square pyramidal coordination, and Mn⁹⁺ is more stable in the octahedral coordination. Though Mn⁷⁺ can retain the tetrahedral configuration (see for instance Fig. 1b and c), its tendency to adopt other environments could be assisted by the Li-vacancy ordering. In short, we suggest that the disappearance of the tetrahedral environment of the manganese upon Li removal explains the observed poor reversibility and/or capacity fading of Li₂MnSiO₄ electrode materials.

<table>
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<th>Oh (Dq units)</th>
<th>Th (Dq units)</th>
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<td>-6</td>
<td>-4</td>
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<tr>
<td>Mn⁷⁺</td>
<td>-10</td>
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**Table 1** Crystal field stabilization energy (CFSE) for Mn ions in square pyramid (SP), octahedral (Oh) and tetrahedral (Th) environments.

(B) Crystal structure and energetics of substituted Li₀.₇₅Mn₀.₂₅M₀.₅SiO₄

The trend of Mn⁵⁺ and Mn⁷⁺ to adopt environments other than tetrahedral geometry is inherent to the nature of those ions. Yet we cannot discard that structural changes of Li₂MnSiO₄ could be ameliorated by cation substitution. Starting from the relaxed ground state of Li₁₂MnSiO₄ and Li₀.₇₅Mn₀.₂₅SiO₄ we have partially substituted 25% of Mn ions for Mg, Fe, Co and Ni. Such cations, together with Zn, are present in tetrahedral LiₓPO₄-type compounds. In a previous investigation we found that for the LiₓMSiO₄ polymorphs, Fe, Mn and Ni stabilize the 2D-Pmmn²¹ structure, while Co and Mg are more stable in the 3D-Pbnm² structure. This selection of cations with different electronic configurations and polymorphic stability offers a wide view of possible substituents for Mn ions in Li₂MnSiO₄.
In the Li$_6$Mn$_3$MSi$_4$O$_{16}$ cell, there are two distinct configurations to accommodate the Li$_{1.5}$Mn$_{0.75}$M$_{0.25}$SiO$_4$ stoichiometry. All the optimized configurations contain Mn and M ions in tetrahedral coordination, with similar deviation from orthogonal symmetry to Li$_{1.5}$MnSiO$_4$ (γ ≈ 93°). The Mg, Co and Ni substituents are in a divalent state (M$^{2+}$), coexisting with 25% Mn$^{2+}$ and 50% Mn$^{3+}$. In Li$_{1.5}$Mn$_{0.75}$Fe$_{0.25}$SiO$_4$ the charge distribution is 25% Fe$^{3+}$, 25% Mn$^{3+}$ and 50% Mn$^{2+}$. The cell volume follows the trend of the ionic radii of the present divalent cations: V$_{Mn^{2+}}$ > V$_{Co^{2+}}$ > V$_{Mg^{2+}}$ > V$_{Ni^{2+}}$. In short, at this level of delithiation all the substituents retain the structural integrity of the lithiated phase.

In the unit cell of Li$_2$Mn$_4$Si$_4$O$_{16}$ there are four distinct configurations to accommodate the Li$_0.5$Mn$_{0.75}$M$_{0.25}$SiO$_4$ stoichiometry. Fig. 4 compares the relative total energy of the four optimized configurations, labelled as 1, 2, 3 and 4. The most stable configuration for each M has been set at the zero energy. In all these configurations, we have analysed the coordination number and the net spin around M ions (Table 2 and Fig. 2 in the ESI†). We found that Mn ions may adopt coordination numbers of 4, 5 and 6, with the latter being restricted to the 4+ oxidation state. Configurations possessing Mn ions in tetrahedral coordination are indicated by a pink circle in Fig. 4. Configurations where octahedral Mn$^{4+}$ is present are denoted by cyan rectangles.

For a given M, the energy difference between configurations can be as large as 0.25 eV per f.u. As seen in Fig. 4, the tetrahedral configuration for all Mn ions destabilizes the structures, while those configurations with Mn$^{4+}$ in octahedral coordination are the most stable. The relative stability certainly depends on the nature of the M ion; the most stable configurations are 1 for Mg, 2 for Ni and 3 for Fe and Co. Fig. 5 shows the optimized most stable structure for each TM, with the atomic distances given in Table 2 in the ESI.† Clear distortions are observed, with none of the substituents retaining the tetrahedral-based framework of the pristine compound. Deviations from the orthogonal symmetry are similar to those observed in the unsubstituted Mn phase (α = 85°, β = 90°, γ = 75°).

For Fe and Co substituents (Fig. 5a–c) possess Mn$^{4+}$ in octahedral coordination, sharing edges with the adjacent Si and Mn polyhedra. Ni is the only investigated TM ion which does not produce octahedral Mn$^{4+}$ in any configuration. Indeed, as seen in Fig. 4, configurations 1, 3 and 4 consist of tetrahedral Mn ions. The most stable configuration (Fig. 5d) is built up by Mn ions in five-fold coordination (see Table 2 in the ESI†), having edge sharing Mn–Mn contacts. Even if Mn$^{4+}$ ions are more stable in octahedral coordination (Table 1), the effect of the Ni$^{2+}$ substituent is to stabilize Mn$^{4+}$ in five-fold coordination. This suggests that Ni$^{2+}$ might be an efficient substituent to ameliorate the structural distortion. All the substituted Li$_{0.5}$Mn$_{0.75}$M$_{0.25}$SiO$_4$ compounds have greater volume than the Mn only parent compound, among them Ni produces the largest cell (76.1 Å$^3$).

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**Table 2** Cell parameters (in Å) of as-prepared Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$ with $x = 0, 0.1, 0.2$

<table>
<thead>
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<th>x</th>
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<th>b</th>
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Fig. 4 Calculated total energy difference for the four Li$_{1.5}$Mn$_{0.75}$M$_{0.25}$SiO$_4$ configurations investigated with M = Mg, Fe, Ni and Co. Pink circles/cyan rectangles indicate structures where tetrahedral/octahedral Mn ions are detected.

Fig. 5 Ground-state geometries of Li$_{0.5}$Mn$_{0.75}$M$_{0.25}$SiO$_4$ (a) M = Mg, (b) M = Fe, (c) M = Co and (d) M = Ni. Color code: Li, green; Mn, pink; M, yellow; and Si, blue.
This is not surprising since Li$_{0.5}$Mn$_{0.75}$Ni$_{0.25}$SiO$_4$ comprises non-oxidized Ni$^{2+}$ ions (see ESI†). The larger volume of the delithiated phase is beneficial since it implies a lower volume contraction respective to the initial phase.

Ni is a possible candidate to ameliorate the structural distortion suffered by Li$_2$MnSiO$_4$ due to the oxidation of Mn$^{2+}$ to Mn$^{4+}$ upon delithiation. Previous DFT work predicts that Li$_2$NiSiO$_4$ has very high de-intercalation voltages, 4.5 V for the Ni$^{2+}$/Ni$^{3+}$ couple and 5.2 V for the Ni$^{3+}$/Ni$^{4+}$ couple. We can thus expect that Ni substitution would increase the average de-insertion voltage of Li$_2$MnSiO$_4$. Even though achieving the full capacity of Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$ electrode materials would be impracticable, they might display better capacity retention upon cycling than Li$_2$MnSiO$_4$.

(C) Experimental investigation of Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$

Fig. 6 shows the XRD patterns collected from as-synthesized Li$_2$MnSiO$_4$ and the substituted Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$ samples with $x = 0$, 0.1, and 0.2. A close view of the (011) peak at about 24.25 degrees of $x = 0$, 0.1, 0.2 showed Vegard’s shift due to Ni substitution. The refined lattice parameters are given in Table 2; a decrease can be seen in all three lattice parameters (see also Fig. S3†). The parameter decreases are expected, as Ni$^{2+}$ in a tetrahedral configuration has a smaller ionic radius than Mn$^{2+}$ in a tetrahedral configuration. For the nominal composition of Li$_2$Mn$_{0.9}$Ni$_{0.1}$SiO$_4$ the ICP analysis yields Ni and Mn contents of 0.0944 ± 3.6%, and 0.9056 ± 3.6%, respectively. The Ni/Mn content in Li$_2$Mn$_{0.8}$Ni$_{0.2}$SiO$_4$ has also been confirmed by ICP analysis (Ni: 0.218 ± 1.7%, Mn: 0.782 ± 1.7%). Attempts to prepare Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$ samples with higher $x$ contents were unsuccessful.

Fig. 7 shows the SEM of the Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$ samples with $x = 0$, 0.1 and 0.2. They all contain aggregates of small rounded particles. The average particle size is about 100 nm for $x = 0$ and 0.1. For $x = 0.2$, some larger plate-like particles are distinguished in the spherical aggregates. Regardless of the small particle size, the as-prepared samples displayed a poor electrochemical behaviour (see Fig. 4 in ESI†), making carbon coating a necessary treatment. Examining the XRD patterns of the carbon coated samples (shown in Fig. 5 of ESI†) the formation of a second phase is observed; due to the reducing conditions Ni has segregated from the samples, as evidenced by the peaks at about 45 and 52 degrees which are attributable to Ni metal (ICSD Collection Number #41508). We cannot ensure that the segregation of Ni from the sample is complete; hence some Ni may remain in the structure. In short, the real Ni content in Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$ carbon coated materials is unknown.

The electrochemical behaviour of the Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$ coated samples is shown in Fig. 8a–c. As evidenced in Fig. 2, regardless of the carbon coating, the prepared Li$_2$MnSiO$_4$ electrode suffers from an important polarization, hence showing a lower specific capacity than that found in ref. 24. Nevertheless, in all the Li$_2$Mn$_{1-x}$Ni$_x$SiO$_4$ materials, the voltage profile changes...
from the first to the second charge which is indicative of major crystal structure modifications. The first charge capacities are 150 mA h g⁻¹ for x = 0, 180 mA h g⁻¹ for x = 0.1 and 250 mA h g⁻¹ for x = 0.2. The increasing capacity with the nominal Ni content in the sample suggests that some of the Ni might remain in the silicate structure. However, as discussed below, we cannot exclude that part of the delivered capacity is due to electrolyte decomposition.

Fig. 9 shows the capacity retention with cycling of Li₂Mn₁₋ₓNiₓSiO₄ coated samples. The materials are able to show reversible capacities exceeding 100 mA h g⁻¹ after the first discharge and stable charge and discharge capacities for the first 10 cycles. This reversible capacity corresponds to the cycling of 0.7 Li ions in Li₁ₓMnSiO₄, consistently with the computational results evidencing that major structural rearrangement has already occurred at half delithiation. No improvement is observed for the Ni doped samples, which is likely due to its segregation from the crystal structure.

**Ex situ XPS** spectra were collected during the initial charge of a Li//Li₁ₓMn₀.₉Ni₀.₁SiO₄ cell at the pristine state, charged to 4.5 V and charged to 4.8 V (see Fig. 6 in the ESL). Fig. 10 shows the collected spectra of Mn₂p, Ni₂p, C₁s, and Si₂p. The Mn₂p₃/₂ peak is made of two components corresponding to Mn²⁺ at 643.0 eV and Mn³⁺ at 646.5 eV. During charging, the intensity of the Mn³⁺ peak decreases while the intensity of the Mn²⁺ peak increases indicating oxidation of Mn on the surface of the material. However, the Ni 2p peak does not change during charging likely due to Ni precipitation as metallic nanoparticles. The C 1s spectra show signals typical of composite electrode materials including adventitious carbon at 284.6 eV, CH₂ bonds at 285.3 eV and CF₂ bonds at 290.7 eV due to the PVdF binder. There is a gradual increase in the intensity of the 287.2 eV peak which is due to (C–O) bonds corresponding to electrolyte decomposition. (d) The Si 2p spectra show a 102.9 eV peak for the Si–O bond in the silicate structure; but after charging, a new peak at 106.4 eV appears which corresponds to Si–F bonds.

**Fig. 10** Ex situ XPS collected during the first charge of a Li cell bearing Li₁ₓMn₀.₉Ni₀.₁SiO₄ as the positive electrode at pristine, charged to 4.5 V and charged to 4.8 V state of charge. (a) The Mn 2p spectra show a gradual tradeoff between Mn³⁺ at ~646.5 eV and Mn²⁺ at ~643.0 eV. (b) Ni 2p spectra do not change at all most likely due to its precipitation as metallic Ni nanoparticles. (c) C 1s spectra show typical peaks at 284.6 eV for adventitious carbon (C–C, C–H), PVdF binder peaks at 285.3 eV for (CH₂), and 290.7 eV for (CF₂). There is also a gradual increase in intensity of the C 1s peak at 287.2 eV which is due to (C–O) bonds corresponding to electrolyte decomposition. (d) The Si 2p spectra show a 102.9 eV peak for the Si–O bond in the silicate structure; but after charging, a new peak at 106.4 eV appears which corresponds to Si–F bonds.

Li₂Mn₁₋ₓNiₓSiO₄ samples confirm the oxidation of Mn²⁺, inactivity of Ni, and possible surface reactions between the SiO₄ framework and the electrolyte.

**Conclusions**

First principles calculations have been utilized to rationalize the poor electrochemical performance of Li₂MnSiO₄. A large number of 142 Li₂MnSiO₄ configurations have been examined. Computational results demonstrate that important crystal structure modifications in the Li₂MnSiO₄ electrode material have already occurred at half delithiation. The irreversible structural changes are linked to severe local distortions around the Mn⁴⁺ polyhedron upon delithiation. Since the lost of tetrahedral coordination of Mn⁴⁺ is rooted in the crystal field stabilization of Mn⁴⁺ and Mn⁵⁺ in higher coordination numbers, such structural distortions cannot be avoided. This explains the difficulties in (i) extracting more than one Li ion from Li₂MnSiO₄ and (ii) holding the capacity retention with cycling even for the first electron process. In this sense, Li₂MnSiO₄ is not competitive as the positive electrode material in Li cells. Yet we have investigated if crystal structure distortions during the charge of the cell could be minimized by partially substituting Mn ions with Mg, Fe, Co and Ni. We infer...
that among these substituents, only Ni would barely help to ameliorate the structural distortion upon lithium de-insertion.

Ni substitution of Mn in Li2Mn1-xNi2SiO4 was successfully achieved up to x = 0.2 by solvothermal synthesis. To make the materials electrochemically active, carbon coating was necessary. The reducing conditions of the carbon coating precipitation as Ni nanoparticles. Li2Mn1-xNi2SiO4 materials, and its precipitation as Ni nanoparticles. Li2Mn1-xNi2SiO4 materials display a good capacity retention with cycling, but limited to only 100 mA h g⁻¹ (0.7 Li ions in Li2MgSiO4), as encountered in the parent Li2MnSiO4. The poor electrochemical behaviour of Li2Mn1-xNi2SiO4 is attributed to the almost total segregation of Ni²⁺ from the silicate structure.

Based on the computational results we discarded Mg, Fe and Co as possible Mn substituents to enhance the electrode characteristics of Li2MnSiO4. On the contrary, DFT calculations suggest that Ni⁵⁺ could help to retain the crystal structure of charged Li2MnSiO4 electrodes, improving the specific capacity delivered by the electrode and its retention with cycling. However, our experimental approach failed to retain Ni²⁺ in the initial Li2Mn1-xNi2SiO4 crystal structure during the conforma-
tion of the electrode. Further work is needed to modify the carbon-coating conditions. In addition, future work combining experiments and calculations is desirable to screen for other chemical modifications likely to improve the electrochemical performance of Li2MnSiO4.

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