

A Quantum Leap Forward for Li-Ion Battery Cathodes

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Investigators

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Abstract

During the three years that have elapsed since proposing this project, the urgency of the need for *improved high-power Li-ion batteries* - especially for use in plug-in hybrid electric vehicles (P-HEVs) – has become ever more poignant. An enormously increased awareness worldwide that greenhouse-gas (GHG) emissions must be dramatically reduced has transformed what was earlier seen as a widely felt need to what has today become an absolute essentiality. Improved environmentally friendly, low-cost, high energy- and power-density upscaled Li-ion batteries with long cycle-life over a wide-range of temperatures must be developed. The express goal of this project is therefore to probe whether silicate-based cathode materials (*e.g.*, Li_2MSiO_4 , where M is some transition metal) can be realistic alternatives, by virtue of their potential to extract >1 electron per 3d-metal, and thereby exceed 200 mAh/g in capacity. A number of modified transition-metal silicate-based cathode materials where have been synthesized based on a DFT-calculation based pre-screening procedure. The electrochemical performance of the materials which emerge has been assessed – first broadly then later in detail - especially in terms of their lithium storage capacity and electrochemical cyclability. Two general types of conclusion can be drawn; the first emerges from *the DFT calculations*:

- Tetrahedral silicate structures are much "softer" than olivines (*e.g.*, LiFePO_4) or spinels (*e.g.*, LiMn_2O_4), rendering them more tolerant to Li-insertion/-extraction strain.
- The now well-established decrease in intercalation voltage from 3.10V to 2.85V during the first cycle of $\text{Li}_2\text{FeSiO}_4$ results from the stabilization of the Li/Fe site-mixing process.
- *Mn substitution* into $\text{Li}_2\text{FeSiO}_4$ to realize a $>1e^-$ redox reaction results in the paradoxical situation that *at low Mn concentrations*, removal of >1 Li-ion per TM atom occurs at too high a voltage (above 4.7V), while *at high Mn concentrations*, the structure degrades.
- Alternative Mn environments are being sought which better accommodate the multivalency of the Mn ion.
- An optimal Li/Fe cation distribution in the *non-stoichiometric* $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$ system is crucial to reducing its over-potential and improving its charge/discharge efficiency.
- A 12.5% *substitution of VO_4^{3-}* into the SiO_4 sites would appear to result in increased capacity and electronic conductivity. The estimated solubility limit for VO_4^{3-} substitution into $\text{Li}_2\text{FeSiO}_4$ is $\sim 25\%$.

Our *experimental work* has led to the following general conclusions:

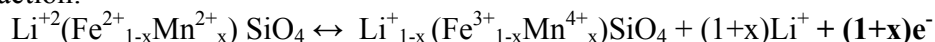
- *Precursor-assisted* methods can be used to prepare $\text{Li}_2\text{FeSiO}_4$ systems. Amorphous assisted synthesis need take no longer than *2 hours* at elevated temperatures. A solid-solution-like sloping plateau is observed in the cycling curves along with good capacity. Alternative low-temperature synthesis methods are also being explored.
- The *non-stoichiometric* $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$ system shows enhanced capacity, combined with less first-cycle Li/Fe site-mixing (as deduced from measured cyclic voltammograms). The non-stoichiometry clearly promotes a faster transition to “lower-voltage behaviour” in the material.
- Both the *Mn and Fe atoms have been confirmed to be redox active* (at ~ 4.0 and 2.8 V, respectively) in Mn-doped $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$; with much improved cycling in the latter case.
- *Polyanion substitution* shows that only low concentrations of VO_4 substitution into the SiO_4 sites can maintain the orthosilicate structure; higher levels of substitution result in phase separation- as confirmed by X-ray diffraction. Electrochemical characterisation of these systems is underway.
- *Cobalt-doping into non-stoichiometric* $\text{Li}_2\text{FeSiO}_4$ has been synthesized successfully and the materials are currently being characterized electrochemically.
- *Modification of the* SiO_4^{4-} *groups in* $\text{Li}_2\text{FeSiO}_4$ *is also underway.* Initial indications are that a glassy-type lithium iron silicate maintains the orthosilicate-type structure. Dimeric silicate groups of type $\text{Si}_2\text{O}_7^{6-}$ are also being studied as potential cathode candidates.
- XPS has proven to be a hugely powerful tool in analyzing the chemical surface properties of the active electrodes in relation to the totally critical cell-stability issues. A detailed understanding of *Solid-Electrolyte Interphase (SEI) formation* on silicate-based cathodes and the related electrolyte stability has been obtained.
- The stability of the *non-stoichiometric* Li-silicate is excellent; similar to that observed for stoichiometric $\text{Li}_2\text{FeSiO}_4$ cycled in an LiTFSI-based electrolyte.

Introduction

Reduction of GHG emissions from the transport sector worldwide has become one of the most pressing scientific challenges of our generation. On-board battery-storage of electrical energy – conditional on the energy being derived from sustainable power sources (solar, wind, water, ...) – is now seen as a viable long-term solution. However, a major problem remains: we lack *batteries* of sufficient quality to meet this challenge. Current batteries are still inadequate in terms of energy- and power-density, safety, cyclability and cost. Significant breakthroughs especially as regards *the active cathode material* are urgently needed.

This goal of this project is therefore a bold one: we seek *The Holy Grail* of the Battery World - a technology which exploits the ever elusive “>1-electron reaction” to facilitate a dramatic increase in battery, and also one which provides improved power. Our more specific goal is to probe the viability of a revolutionary new family of iron silicate-based active cathode materials to deliver energy- and power-densities well in excess of those available from currently used materials in Li-ion batteries, and (through the use of iron) to be significantly cheaper and more environmentally acceptable.

Silicates are attractive cathode materials since they are intrinsically stable and can accommodate a range of transition-metal (TM) ions. We can substitute Fe (which normally only pass between Fe^{2+} and Fe^{3+}) in the parent material of the family $\text{Li}_2\text{FeSiO}_4$ by some other TM-ion which can undergo X^{2+} to X^{3+} to X^{4+} (*etc.?*) transitions, and thereby facilitate the removal of at least $(2\text{Li}^+ + 2\text{e}^-)$ from the material – with a resulting 100% increase in capacity. The Mn-substituted system $\text{Li}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{SiO}_4$ facilitates the redox reaction:



A schematic of the corresponding charge/discharge curve (*Fig. 1*) illustrates the potential gains to be made for $x = 0.5$. Three advantages open up:

- The theoretical capacity of the resulting material would increase to 255 mAh/g.
- The voltage over 67% of this plateau is raised to lie above 4V.
- Most subtly relevant to EV applications – this entire upper-voltage plateau becomes the range of application in an electric vehicle, despite the base cathode material only having a voltage of *ca.* 2.8V vs. Li/Li^+ .

Note, however, that even the “unsubstituted” green curve can still be exploited to advantage in lower-voltage larger-scale Li-ion batteries for sustainable energy storage.

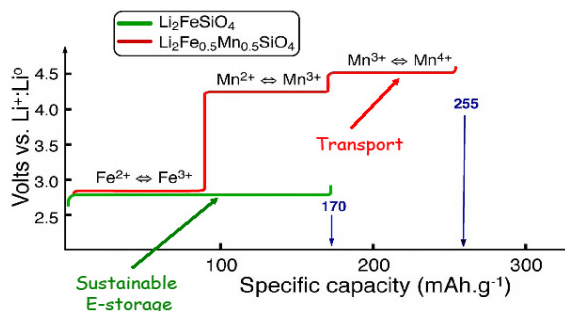


Figure 1: A schematic representation of the capacity gains to be made by replacing 50% of the Fe in $\text{Li}_2\text{FeSiO}_4$ by Mn.

The scientific challenge is then still as defined in the original proposal: to probe what structural/chemical conditions must be created in a material to promote a reversible $\geq \pm 1$ change in the TM-ion oxidation-state of the $\text{Li}_2\text{FeSiO}_4$ cathode material, and to find how we can modify the structural environment of the TM-ions to accommodate these changes.

Background

The wide-scale move towards *low-fuel vehicles* began more than 12 years ago with the introduction onto the open market in 1997 of the THS-based Toyota PRIUS HEV; followed up by the PRIUS II model in 2003. Momentum has been increasing ever since, and many now feel that the corner has already been turned in *the transition from a fossil-fuel based to an electricity-based transport system*, especially in the small-car range. Any car producer who wishes to survive the current crisis must move seriously into the

development of HEV/Plug-In HEV/EV concepts for general release as soon as possible. However, *an optimal battery* (now destined to be of Li-ion type) *has yet to emerge to drive this development forward* and, furthermore, the feature most lacking in this development is *a truly viable cathode material* for these batteries. The current status of battery development for transport applications can be summarized in this way:

- **HEVs:** where braking-energy is stored in on-board batteries; *cf.* the Toyota PRIUS and the Honda INSIGHT. Ni-MH will almost certainly soon be replaced by Li-ion batteries. *An on-board auxilliary battery in some form of hybrid concept could soon become standard in all vehicles.*
- **Plug-in HEVs:** use overnight (off-peak) grid power to charge a considerably larger battery than an HEV battery. This fully charged battery serves as the power source (over the first 30-50 miles) until HEV-mode cuts in. It is estimated that this “cut-in” stage will never be reached in the majority of trips made today in the United States.
- **Pure EVs:** use no other back-up motor. The battery is charged when necessary. It is not clear today whether such vehicles will appear on the general market, but rather for niche applications.

One thing is clear, however: Europe and the United States lie way behind Asia in this area, and huge investments are needed to catch up. This will not be easy during the current economic freeze! The current status of *cathode development* for these up-scaled Li-ion batteries can best be summarized as follows:

- **Capacities must be doubled** – to reach *ca.* 300 Ah/kg. This is the precise goal of this present project *via* our hunt for an ideal >1 el. reaction!
- Large-scale batteries mean that **Fe and Mn** (possibly V) **are the only realistic TM candidates**. As regards specific materials: *LiFePO₄* has its limitations, related to there only being 1 Li per TM atom in the formula, while the layered *LiNi_xMn_yCo_zO₂* materials can also have a cost problem. Nickel is also an environmental hazard in larger quantities.
- **Lower-cost large-scale synthesis methods** must be found; *hydrothermal synthesis* is the current favorite, but even larger systems must be developed to cope with the volumes anticipated in the coming market.

*** **There are clear opportunities for the Li-Fe-silicates!** ***

Results

Our general approach here has been to combine the judicious use of a Density Function Theory (DFT) based computer-screening procedure with the subsequent use of a range of synthetic and characterization techniques (electrochemical cycling, *in situ* powder XRD and ND, SEM and HR-TEM microscopy, *in situ* Mössbauer and XPS/PES spectroscopies, particle-size and electrode porosity measurements, ...) to probe what structural/chemical conditions are needed to promote a reversible $\Delta > +/-1$ change in oxidation-state in a TM ion. The general project methodology is summarized in *Fig. 2*.

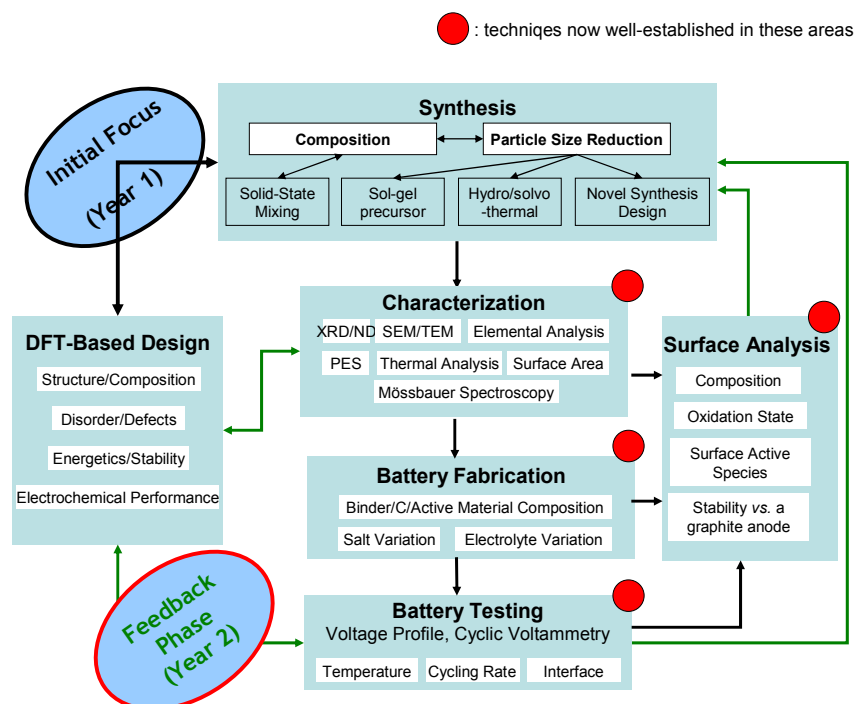


Figure 2: A summary of the general strategy and methodology used in the project.

DFT-based materials design

The different types of possible design modifications used are summarized in *Fig. 3*. Earlier work has shown that a mixing of Li- and Fe-site occupations occurs on cycling $\text{Li}_2\text{FeSiO}_4$. Mixing Li- and M-site site-occupancy in pristine Li_2MSiO_4 has thus been tested in calculations to assess the possibility of: (i) increasing the electronic conductivity by creating M-O-M linkages (M are otherwise separated from one another by SiO_4^{4-} groups); (ii) transforming a 2- into a 3-dimensional Li-ion conducting network by “activating” ion-conduction pathways along the third direction (the *b*-axis); (iii) optimizing the intercalation voltage. The M-O-M linked structures calculated were found to be only 0.15-0.20 eV/formula unit (f.u.) higher in energy than the original $\text{Li}_2\text{FeSiO}_4$ structure. Partial mixing to create finite $-(\text{O-M})_n$ -sequences gives lower energy, *ca.* 0.07-0.17eV/f.u. The effect of structural modulation in the direction of the cation coordination tetrahedra on Li-ion conductivity has also been studied. This modulation distinguishes the β - and γ -phases of Li_3PO_4 , the parent structure to Li_2MSiO_4 , and leads to very different Li-ion conductivities in these phases [1]. The Li-/M-cation distribution was found to change the intercalation voltage (*Fig. 4*). The reported $\text{Pmn}2_1$ structure [2] and the recently reported modulated $\text{P}2_1$ structure [3] are slightly more stable than the β - $\text{Li}_2\text{CoSiO}_4$ structure – which corresponds to the situation where 100% of the Fe and Li site-occupations are reversed. This structure is stabilized by $\sim 0.23\text{eV/f.u.}$ on delithiation with a corresponding lowering of the voltage. This explains the decrease of intercalation voltage from 3.10V to 2.85V during the first cycle [4], and gives an insight into the extent of structural and energetic changes occurring in these intercalation hosts.

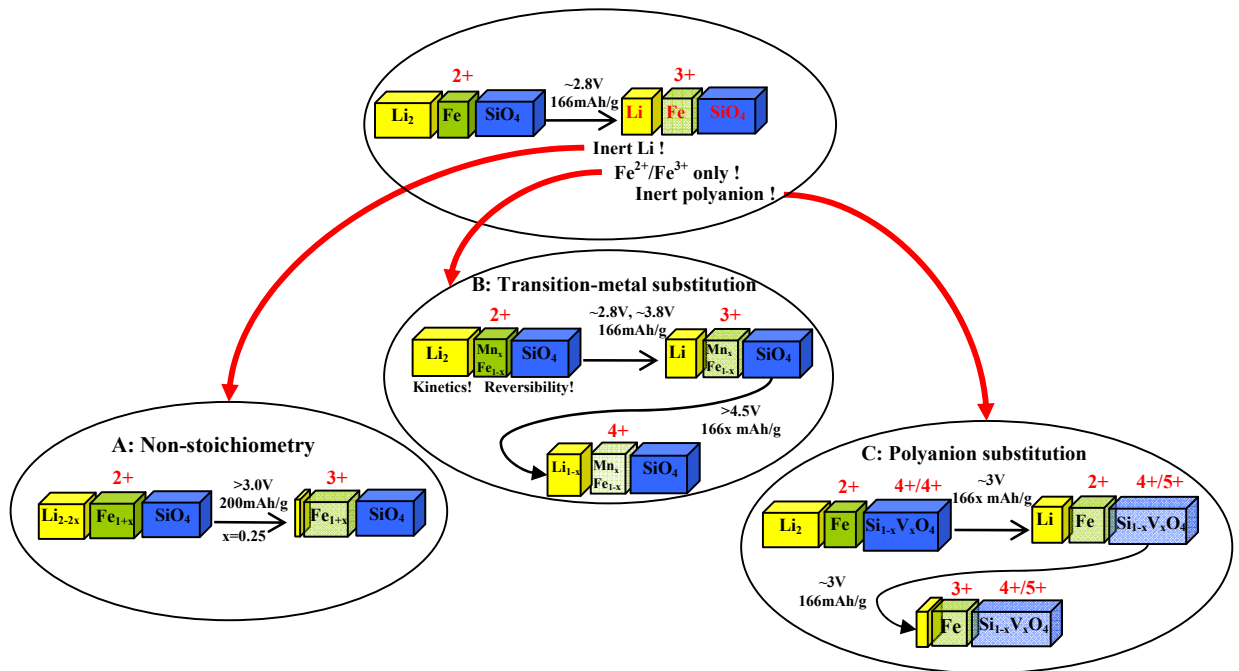


Figure 3: A schematic of the materials design strategy exploited in the project.

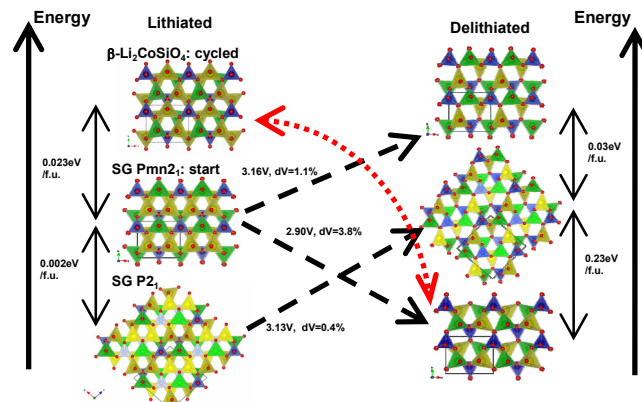


Figure 4: Calculated Li-extraction voltages for $\text{Li}_2\text{FeSiO}_4$ for different Li/Fe-mixing modes and modulation of the coordination polyhedra: *left* - lithiated phases; *right* - delithiated phases. Li de-intercalation voltages (going from *left* to *right*) are also shown. The dashed red arrow shows the charge-discharge route after the first-cycle phase transition.

- *Non-stoichiometric systems:* $\text{Li}_{2-2x}\text{M}_{1+x}\text{SiO}_4$, $\text{M}=\text{Fe}, \text{Mn}$ (Strategy A: Fig. 5)

Earlier calculations promised increased capacity through the higher Fe:Li ratio and higher electron conductivity due to the -Fe-O-Fe- pathways. However, $> 4\text{V}$ is needed to remove the final 0.25 Li ions on a deep delithiation of $\text{Li}_{1.5}\text{Fe}_{1.25}\text{SiO}_4$. Charge density analysis also showed that less electrons could be extracted from these deformed sites. An optimal Li/Fe distribution is thus crucial to minimizing the charge/discharge efficiency.

- Mn-substitution into $\text{Li}_2\text{FeSiO}_4$ (Strategy B: Fig. 5)

Experimental and theoretical work [5-8] combine to reveal two major problems relating to Mn-based materials: (i) structural degradation on deep delithiation, resulting in capacity loss; (ii) poor kinetics. At low Mn-concentrations, the calculated oxidation of Mn^{3+} to Mn^{4+} occurs at >4.7 V, suggests that the formation of an Mn^{4+} hole-polaron with compensating Li-vacancy is energetically unfavourable [5]. This is observed as progressive polarization on deep delithiation, and can imply that Mn substitution into $\text{Li}_2\text{FeSiO}_4$ could prove to be a dead-end in our search for a means of enhancing the capacity in $\text{Li}_2\text{FeSiO}_4$ through the removal of $>1\text{Li}^+$ ion per f.u.

- Polyanion doping (Strategy C: Fig. 5)

VO_4^{3-} substitution for SiO_4^{4-} in $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$ has been calculated for 12.5% and 100% substitution to investigate the effect of both concentration extremes. The VO_4 polyanion can be electrochemically active in the 100% substituted case at a low 2.1 V (Fig. 5: left). The tetrahedral structures are also much softer than olivines and spinels, making them more tolerant to Li-intercalation strain. A 12.5% substitution of VO_4^{3-} into the SiO_4 sites would appear to result in increased capacity and electronic conductivity. The estimated solubility limit for VO_4^{3-} substitution into $\text{Li}_2\text{FeSiO}_4$ is $\sim 25\%$ [6]. See also Fig. 5: right.

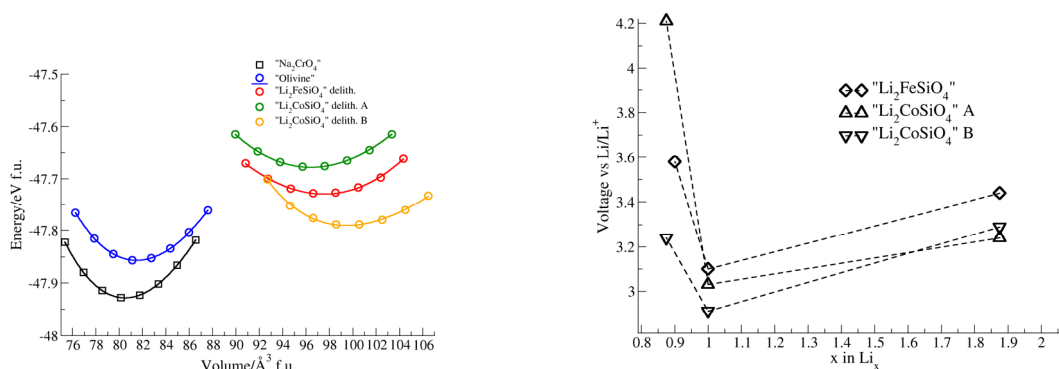


Figure 5: Left: The stability of LiFeVO_4 polymorphs; octahedrally coordinated Fe in olivine (blue); inverse spinel (black); and three tetrahedrally coordinated systems (green, red and orange) (left). Right: Li-intercalation voltages for the 12.5% VO_4 -substituted $\text{Li}_2\text{FeSiO}_4$ polymorphs as a function of Li-concentration.

Synthesis and sample characterization

A range of synthesis methods have been tested during the course of synthesizing the silicate-based materials which emerge from our DFT-screening procedure. It is very clear, from an industrial production viewpoint, that huge gains in time and economy can be made through a carefully selected and system-tuned synthesis technique. It is found that a final heating step at $> 600^\circ\text{C}$ is usually necessary in both solution-based and solid-state techniques to form the final product. However, the precursor preparation step to obtain well-mixed reactive starting materials is totally essential to produce the desired material.

To exemplify: an assisted method was used for the precursor preparation for $\text{Li}_2\text{FeSiO}_4$. A final product (particle-size: *ca.* 100 nm) was readily obtained through heat treatment at 700 °C for a wide range of heat-treatment times; the samples contained trace amounts of impurity, *e.g.*, SiO_2 .

The corresponding electrochemical profiles of the resulting $\text{Li}_2\text{FeSiO}_4$ (Fig. 6) show the material to be electrochemically active, with the typical voltage-drop feature from 3.1 to 2.8V after the first charge-cycle. Fig. 6b shows the discharge cycle for $\text{Li}_2\text{FeSiO}_4$ prepared by different methods; the bulk sample gives a very flat plateau, while samples prepared by the citrate-assisted method show solid-solution behaviour with distinctly sloping curves instead of plateaus. A clear general trend is better electrochemical performance for shorter heat-treatment times.

Experimental studies of *non-stoichiometric* lithium iron silicates have continued [9]. Non-stoichiometric $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$ for $x=0.25$ (theoretical capacity ~ 200 mAh/g) shows different redox behaviour compared to $\text{Li}_2\text{FeSiO}_4$ (Fig. 7). The non-stoichiometry clearly promotes a faster transition to “lower-voltage behaviour” in the material. Moreover, there are indications that Fe on the vacant Li-site can increase Fe-O-Fe connectivity and thereby improved the conductivity of the material. Both $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_{1.5}\text{Fe}_{1.25}\text{SiO}_4$ show good capacity retention during the first charge-discharge cycle. Moreover, a small

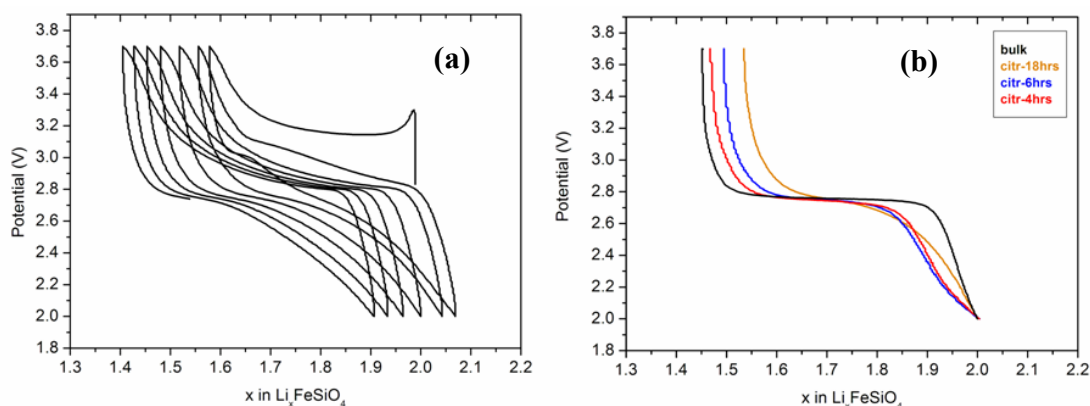


Figure 6: (a) Electrochemical cycling curves; and (b) typical discharge curves for $\text{Li}_2\text{FeSiO}_4$ prepared by the assisted method using different heat-treatment times.

second plateau was observed for non-stoichiometric $\text{Li}_{1.5}\text{Fe}_{1.25}\text{SiO}_4$ between 3.5 V and 3.7 V during charging. This is probably due to a different environment for some of the Fe, coupled to solid-solution behaviour. The discharge capacities for $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_{1.5}\text{Fe}_{1.25}\text{SiO}_4$ are 90 mAh/g and 100 mAh/g, respectively, in our so far grossly unbalanced test cells. A very encouraging result!

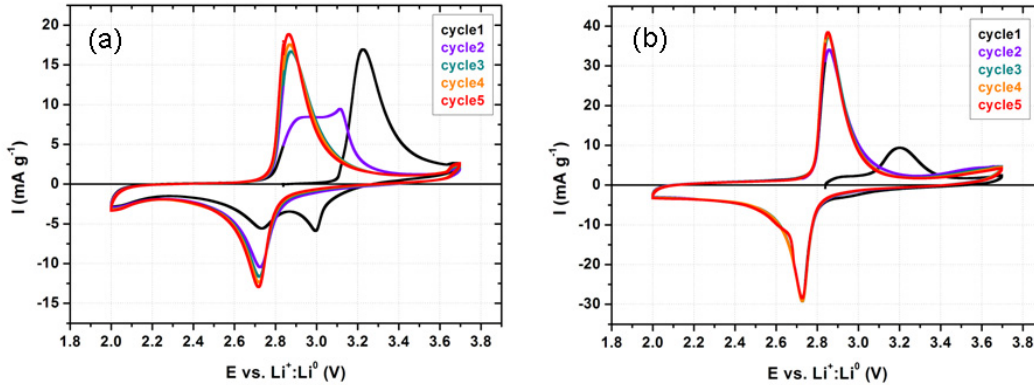


Figure 7: Cyclic voltammetry scans for (a) $\text{Li}_2\text{FeSiO}_4$ and (b) $\text{Li}_{1.5}\text{Fe}_{1.25}\text{SiO}_4$.

Attempts to prepare the “symmetric” $\text{Li}_{1.33}\text{Fe}_{1.33}\text{SiO}_4$ compound show initially that the material contains significant amounts of impurities (including residual carbonates and other higher-valence iron oxides). Its electrochemical performance also shows large irreversible capacity fade during cycling; probably a result of side reactions involving these impurities.

The Mn-doped $\text{Li}_2\text{Mn}_{0.1}\text{Fe}_{0.9}\text{SiO}_4$ system was earlier known to facilitate additional lithium extraction by utilizing the $\text{Mn}^{2+} \leftrightarrow \text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+}$ redox pathway. The first charge cycle clearly shows the oxidation of reaction from Mn^{2+} to Mn^{3+} at 4.1 V, but this slowly disappears on subsequent cycling. We have prepared $\text{Li}_{1.5}\text{FeMn}_{0.25}\text{SiO}_4$ [10] to ascertain whether greater stability can be achieved in a non-stoichiometric analogue. Cycling curves (*Fig. 8*) shows the oxidation process from Mn^{2+} to Mn^{3+} clearly visible at $\sim 4.0\text{V}$. The $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ reaction clearly recurs in successive charge cycles of the non-stoichiometric mixed Mn-Fe system. In addition, the reduction plateau process for both Mn and Fe appear to occur in the same regime $\sim 2.8\text{V}$, suggesting that a much larger charge-discharge polarization in Mn than in Fe. An important result !

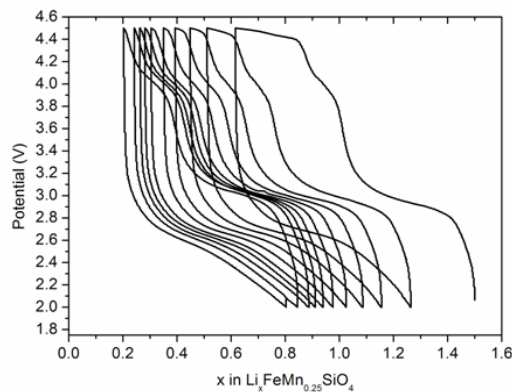


Figure 8: Electrochemical profile of $\text{Li}_{1.5}\text{FeMn}_{0.25}\text{SiO}_4$.

A $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$ plateau is also evident $\sim 4.4\text{V}$ during the first charge-cycle, but the drops sharply on discharge, and the subsequent charge-cycles show that this plateau slowly disappears after 5 cycles, reminiscent of what was seen earlier for the

stoichiometric $\text{Li}_2\text{Mn}_{0.1}\text{Fe}_{0.9}\text{SiO}_4$ case. We have also studied whether the use of a “by-stander ion” such as Mg can help improve the electrochemical cycling of $\text{Li}_2\text{MnSiO}_4$. While $\text{Li}_2\text{Mg}_{0.125}\text{Mn}_{0.875}\text{SiO}_4$ was synthesized successfully, though with some MnO impurity, it exhibited poor electrochemical performance with little reversibility.

Mössbauer spectroscopy studies of *stoichiometric* $\text{Li}_2\text{Mn}_{0.125}\text{Fe}_{0.875}\text{SiO}_4$ showed evidence of ferric components coexisting with ferrous; only one component for the 10% Mn-doping case, but two for the 25% Mn-doping case. These components show hyperfine parameters representative for four-coordinated Fe^{3+} ions [11]. *Non-stoichiometric* $\text{Li}_{1.5}\text{Fe}_{1.25}\text{SiO}_4$ showed essentially equivalent results, as indeed did the *Mn-doped non-stoichiometric* $\text{Li}_{1.5}\text{FeMn}_{0.25}\text{SiO}_4$. This ferrous signal can be assumed to emanate from Fe-ions occupying Li-sites, suggesting that about 10% of the Fe atoms substitute for Li both when there are excess of Fe or excess of Mn but with Li deficiency. The question as to whether Mn also substitutes for Li in the *non-stoichiometric* $\text{Li}_{1.5}\text{FeMn}_{0.25}\text{SiO}_4$ case must be left open for the moment. It is remarkable, however, that the Fe spectral intensities are roughly the same for the two non-stoichiometric samples, suggesting that the excess Mn in $\text{Li}_{1.5}\text{FeMn}_{0.25}\text{SiO}_4$ is distributed in statistically the same manner as the Fe atoms over the Li- and Fe-sites in the structure.

XPS interface stability studies

The surface chemistry of the pristine *non-stoichiometric* $\text{Li}_{1.5}\text{FeMn}_{0.25}\text{SiO}_4$ powder, the composite electrode after the contact with electrolyte (at OCV) and under different states of charge has been analyzed by careful X-Ray Photoelectron Spectroscopy (XPS). The relevant XPS data are shown in *Fig. 9*.

No indication of any degradation reactions can be observed in the Si2p peak for this non-stoichiometric material. Moreover, after contact with the electrolyte, the C1s spectrum remains essentially unchanged; only a very small amount of carbonate species seem to be formed ($E_B = 289.7\text{eV}$). Nor does charging the battery to 3.7V appear to change the spectrum significantly. However, increasing the potential to 4.2V results in solvent decomposition reactions, as reflected in the changes in the spectral shape of the C1s emission. Evidence of a polymerization reaction of EC at higher potentials is also found. A similar observation of this ongoing decomposition reaction is observed at 4.4V. Even larger quantities of degradation products can be observed on discharging to 3.0V. On the other hand, the LiBOB salt does not seem to be affected by this reaction. The B1s peak at $E_B = 193.2\text{eV}$ exhibits no changes for the different states of charge of

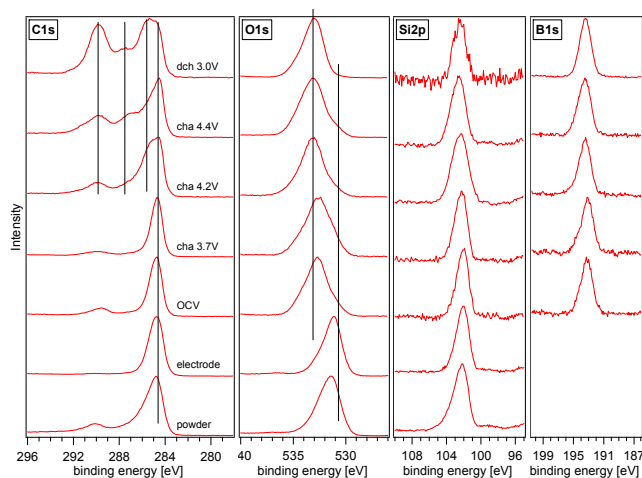


Figure 9: XPS spectra for non-stoichiometric $\text{Li}_{1.5}\text{FeMn}_{0.25}\text{SiO}_4$ composite electrodes under different states of charge; a LiBOB-based electrolyte mixture has been used.

the $\text{Li}_{1.5-x}\text{FeMn}_{0.25}\text{SiO}_4$ electrode; this is a clear indicator of salt stability. The C1s core-level emission also suggests solvent instability at higher potentials, forming an SEI-type surface layer. These species react further under discharge during the transfer of Li^+ species from the liquid phase to the solid. The O1s emission confirms these findings. After contact with the electrolyte and on charging, the relative intensity of the oxygen peak in the silicate material is reduced more and more, and finally disappears completely after discharge.

To summarize, at potentials around 4.2-4.4V, *solvent* degradation reactions occur resulting in additional surface species on the cathode. There are, however, no indications of *salt* decomposition or *electrode* degradation. The stability of non-stoichiometric Li-silicate is therefore excellent and, indeed, similar to that observed for stoichiometric $\text{Li}_2\text{FeSiO}_4$ cycled in a LiTFSI-based electrolyte [12].

Future directions – DFT-based prediction

What we have learnt so far then is that dramatic structural changes can ensue in the course of multi-electron processes when large changes in Li-ion content take place. The channels accommodating the Li-ions tend to collapse or become blocked by the TM-ions when the Li-ions are extracted. We must therefore continue our efforts to seek a better balance between the guest TM- and the polyanions for the purpose of stabilizing the $\text{Li}_2\text{MnSiO}_4$ structure. Analogous to earlier reported pyrophosphates [13], some pyrosilicates can prove to fulfil the above set of criteria and are currently under both theoretical and experimental investigation.

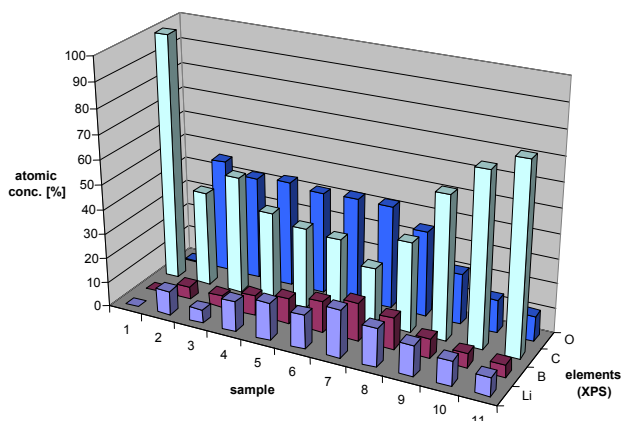


Figure 10: The relative concentrations of Li, B, C and O on the surface of carbon anodes after cycling in a 3-electrode cell, as ascertained by *post mortem* XPS analysis; Ar-ion sputtering times increase from left to right. A LiBOB salt was used for these studies, which were made at 60°C.

Future directions – experimental work

Given that the silicates only appear to cycle with moderately impressive electrochemical performance, we are prompted to attempt to find ways of improving the rate/kinetics of the materials – as well as find ways of achieving full reversibility in the utilization of the lithium in the structure. We are currently turning our attention to the following approaches:

- *Polyanion substitution:* This has two functions; it improves electronic conductivity and can provide redox-active species to facilitate Li-ion transport. We began by substituting 50% of the PO_4^{3-} ions in the $\text{Li}_2\text{MnSiO}_4$ structure by SiO_4^{4-} ions, but this led to phase-separation into an orthosilicate, MnO and Li_3PO_4 . Similarly, 50% substitution by VO_4^{3-} into the same structure resulted in mixtures of MnO, Li_3VO_4 and SiO_2 . This suggests the introduction of lower concentrations of these substituents. The XRD pattern for $\text{Li}_2\text{Fe}(\text{Si}_{0.875}\text{V}_{0.125})\text{O}_4$ shows the orthosilicate structure to be maintained with only slight unit-cell expansion along the b-axis. Mn^{4+} substitution into the Si-site is also underway to probe its viability.

Conclusions

The reduction in GHG emissions on a global scale from the transport sector has today become one of the most pressing challenges facing our generation. GHGs are predicted to soon account for more than one-third of all CO_2 emissions worldwide! On-board battery-storage of electrical energy - provided that the energy originates from sustainable power sources (solar, wind, water, ...) – is a blatantly obvious solution. The successful development of an *ideal large-scale battery* would have an immense influence on the development of our planet. It is, in fact, hard to explain to the general public just how far-reaching the repercussions of such a battery would be. Ironically, the transition from

a fossil-fuel based to an all-electric economy must take place sooner or later anyway - so why not sooner! Access to fossil fuels is already becoming an ever more expensive luxury as sources deplete slowly but surely. Even at the broader level of energy supply, large-scale battery development is key to GHG emissions, since it will facilitate the global implementation of renewable energy sources.

Publications

1. Larsson, P., Rajeev, A., Liivat, A. and Thomas, J.O., Structural and electrochemical aspects of Mn-substitution into $\text{Li}_2\text{FeSiO}_4$. *Submitted to: Chem. Mater.* 2008.
2. Liivat, A. and Thomas, J.O., DFT-assisted design of orthosilicate-based cathode materials for Li-ion batteries. *Under submission to: Electrochem. Commun.*
3. Kam, K.C., Enslin, D., Liivat, A., Häggström, L. and Thomas, J.O., Enhanced capacity in the non-stoichiometric lithium iron silicate cathode material, $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$. *Ms. in preparation.*
4. Kam, K.C., Enslin, D., Häggström, L. and Thomas, J.O., Manganese substitution into the non-stoichiometric lithium iron silicate cathode material, $\text{Li}_{1.5}\text{Fe}_{1.25-z}\text{Mn}_z\text{SiO}_4$. *Ms. in preparation.*
5. Enslin, D., Stjern Dahl, M., Nyten, A., Gustafsson, T. and Thomas, J. O., A comparative XPS surface study of $\text{Li}_2\text{FeSiO}_4/\text{C}$ cycled with LiTFSI- and LiPF₆-based electrolytes. *J. Mater. Chem.*, 19, 82, 2009.
6. Enslin, D., Jiang, Y., Gustafsson, T., Armand, M. and Thomas, J.O., Electrolyte stability for stoichiometric $\text{Li}_2\text{FeSiO}_4$. *Ms. in preparation.*

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7. Stjern Dahl, M. (PhD Thesis: Sept. 2007) Stability phenomena in novel electrode materials for lithium-ion batteries: ISBN 978-91-554-6969-6; urn:nbn:se:uu:diva-8214.
8. Zakrzewski, P. EuroMaster Thesis: Sept. 2007, The relationship between synthesis parameters, crystal structure and performance in $\text{Li}_2\text{FeSiO}_4$.
9. Jiang, Y., EuroMaster Thesis: Sept. 2008, The rôle of the electrolyte in surface-layer formation on $\text{Li}_2\text{FeSiO}_4$.

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Presentations

1. Getting more capacity out of Fe-based cathodes for HEV-battery applications, Edström, K., Ensling, D., Gustafsson, T. Kam, K. Liivat A. and Thomas, J.O., at the American Automotive Battery Conference (AABC), Tampa, Florida, May 2008.
2. Strategies for optimizing the performance of silicate-based cathodes for Li-ion battery applications, Kam, K., Liivat, A., Gustafsson, T. and Thomas, J.O., at the International Meeting on Lithium Batteries (IMLB2008), Tianjin, China, June 2008.
3. Modelling non-stoichiometry and disorder in silicate-based cathode materials, Liivat, A., Larsson, P. and Thomas, J.O., at the International Meeting on Lithium Batteries (IMLB2008), Tianjin, China, June 2008.
4. Modelling the surface layer on $\text{Li}_2\text{FeSiO}_4$ from systematic XPS analysis, Stjern Dahl, M., Ensling, D., Gustafsson, T. and Thomas, J.O., at the International Meeting on Lithium Batteries (IMLB2008), Tianjin, China, June 2008
5. Optimizing the performance of iron silicate based cathodes for upscaled Li-ion battery applications, Thomas, J.O., at the 49th Battery Symposium in Japan, Sakai, Osaka, November 2008.
6. A quantum leap forward for Li-ion battery cathodes, Edström, K., Ensling, D., Gustafsson, T., Kam, K., Liivat, A. and Thomas, J.O., at the GCEP Research Symposium: "Energy Research – Five Years and Beyond", Stanford University, October 2008.
7. Upscaling the Li-ion battery for sustainable energy storage applications, Thomas, J.O., at ENERGY 2008+, Copenhagen, Denmark, October 2008.
(a pre-conference to the Climate Summit in Copenhagen, December 2009.)

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