A Quantum Leap Forward for Li-Ion Battery Cathodes


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Abstract
Our project focus has been to develop a new silicate-based cathode material for large-scale, environmentally friendly, low-cost, high energy- and power-density Li-ion batteries giving long cycle-life over a wide-range of temperatures. The parent material in this context is Li$_2$FeSiO$_4$ (“LFS” - hereafter). A central goal has been to extract >1 electron per 3d-metal, and thereby achieve a cathode material with capacity well in excess 200 mAh/g – a critical EV-related breakthrough. We have throughout exploited a DFT-modeling based screening procedure – followed by synthesis of the most promising candidate materials which emerge. Earlier screening of this type had suggested three general strategies which could prove fruitful:

A: Non-stoichiometry - for capacity enhancement.
B: TM-ion substitution - for capacity and rate enhancement, and structural stabilization.
C: Polyanion substitution - for capacity and rate enhancement.

A fourth somewhat related approach has latter begun to show promise: the use of standby-ions which do not themselves participate actively in the redox reaction, but perturb the structural situation of the redox active ions themselves.

New theoretical results include Li-ion diffusion data for “un-mixed” and “mixed” Li/Fe-ion systems showing Li$^+$ diffusion to be two-dimensional in the LFS structure. This suggests that Li-insertion/de-insertion kinetics (and hence cathode rate-performance) can be improved if the growth of rod-like particles can be promoted with their diffusion plane perpendicular to the rod axis. It is also found that TM-ions can be incorporated into the non-stoichiometric structure, formulation Li$_{2-2x}$Fe$_{1+x}$SiO$_4$, to give shorter TM-TM ion distances, higher electron-transport rates - and hence higher electronic conductivities. This will most certainly prove to be a key result.

Surprisingly, even 50% substitution of the Mn-site in Li$_2$MnSiO$_4$ by different inert “bystander” ions (Mg, Ni, Zn, Cu, Ca, ...) was found to be unable to suppress the problematical distortion found earlier in the Mn-coordination. The notion thus emerges that such distortion can, in fact, be an essential structural condition for future success. This idea has been fueled by recent interesting results on the LiFePO$_4$ system. Finally; 12.5% substitution of VO$_4^{3-}$ into the SiO$_4$ site in LFS and Li$_2$CoSiO$_4$ results in increased capacity and electronic conductivity. This also gives indications of future research directions.

Synthetic techniques have been developed further: hydrothermal synthesis is now able to give first-cycle capacity as high as 160mAh/g in LFS, with stable cycling at ca. 140 mAh/g and C/20 rate. A solvothermally-assisted sol-gel process has been used successfully to control particle-shape. Solid-state synthesis of LFS was found to be highly sensitive to the type of reducing gas and amount of carbon-additive used. Microwave-assisted synthesis has given dramatically fore-shortened synthesis times: from days to minutes. Materials characterization has shown that:
The bystander-ion system Li$_2$Mn$_{0.5}$Mg$_{0.5}$SiO$_4$ crystallizes in the Li$_2$MgSiO$_4$ structure (SG: P2$_1$/n). This material is electrochemically active, though formed at a ~500 °C lower temperature, as a result of the introduction of the bystander-ion Mg. This material shows promise of becoming the centre of international focus in the development of this whole family of materials.

The non-stoichiometric system Li$_{2-2x}$Fe$_{1+x}$SiO$_4$, $x=0.25$ shows first-cycle capacity of ~200 mAh/g. A tantalizing problem has appeared, however: the family of materials has been shown to be consistently “two-phase” – LFS in coexistence with a so-far unidentifiable together non-crystalline phase, which is providing the additional extra capacity.

Solid-state and hydrothermal synthesis routes have been used in efforts to make the pyrosilicate system Li$_2$Mn$_2$Si$_2$O$_7$. However, only the Na-counterpart is thermodynamically stable; suggesting that a two-step synthesis via Na$_2$Mn$_2$Si$_2$O$_7$, followed by Li$^+$ ion-exchange is needed.

XPS studies have convinced us of the intrinsically high chemical and electrochemical stability of the LFS cathode system – at least equal to that of LiFePO$_4$ (“LFP” – hereafter). Along with “cost”, this is arguably the most attractive feature of the material in terms of its relevance to up-scaled Li-ion battery applications – in combination with its potential for hosting a >1 electron reaction.

Careful pre-cycling of the Li$_2$MnSiO$_4$ system by successively raising the upper cut-off voltage from 3.7 to 4.2 to 4.4 V has also been shown to stabilize the cycling. This is a valuable result in our further understanding of how best to exploit the full potential of the silicates. Recent results suggest that we should perhaps have raised the upper limit to 5V!

Finally; we have successfully demonstrated for the first time (to the best of our knowledge) the cyclability of a Li-ion battery “whole-cell” (with a capacity of ca. 80 mAh) based on an LFS cathode and a graphite anode.

We have subsequently also demonstrated the exciting use of LFS as a valuable voltage marker during the discharge of LFP in EV applications. This is quite obviously a most interesting market application for LFS – perhaps the most interesting at the moment.

Introduction

The worldwide reduction of Green-House Gas (GHG) emissions from the transport sector will remain one of the key scientific challenges of our generation. Despite our continued optimism, a totally sustainable solution could well take the better part of the 21st Century to achieve. Progress in the Battery World has always been notoriously slow - “glacier pace” according to The New York Times! We have been living with the lead-acid battery for almost two centuries. Clearly, on-board battery-storage of electrical energy - originating from sustainable power sources (solar, wind, water, etc.) - constitutes a very obvious component in the long-term solution of the problem. However, even if huge progress is currently being made, it is true to say that we still lack batteries with the necessary performance to meet the challenge. Current large-battery technologies still fall short in terms of energy- and power-density, cyclability, cost and - above all - SAFETY. Important breakthroughs are sorely needed, especially as regards the active cathode material.

This is the specific focus of the present project, where we are seeking to overcome the intrinsic limitation of the “only 1-electron reaction”, and thereby open the door to a dramatic increase in energy-storage capacity and power. Our goal has been to probe the viability of a new family of iron silicate-based active cathode materials for this purpose; i.e., to deliver energy- and
power-densities well in excess of those available from currently used cathode materials in Li-ion batteries. The exploitation of the transition-metal iron (Fe) makes for a significantly cheaper and more environmentally acceptable technology platform – as in the case of LFP. However, the silicates are additionally attractive as cathode materials since they are intrinsically more stable and can accommodate a range of transition-metal (TM) ions. The parent material of the family is LFS, in which only the $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ couple is redox active, and hence only one Li-ion can be removed from the structure during the electrode reaction. The overriding goal of the project is then to devise ways of modifying the structure, so that $>1$ Li-ion can be extracted in the positive electrode reaction of the battery. Typically, if Fe is substituted by some other TM-ion ($X^{2+}$) which can undergo $X^{2+} \leftrightarrow X^{3+} \leftrightarrow X^{4+}$ transitions, this would facilitate the removal of $>1$ Li$^+$ ion from the material, resulting in a corresponding increase in capacity. Illustrating this with the Mn-substitution of the system to (say) $\text{Li}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{SiO}_4$, this would facilitate the redox reaction:

$$\text{Li}^{+2}(\text{Fe}^{2+}_{1-x}\text{Mn}^{2+}_x)\text{SiO}_4 \leftrightarrow \text{Li}^{+1-x}(\text{Fe}^{3+}_{1-x}\text{Mn}^{4+}_x)\text{SiO}_4 + (1+x)\text{Li}^+ + (1+x)e^-$$

This means that (for example) 50% Mn-substitution of the Fe-sites in LFS, i.e., $x = 0.5$ would facilitate three important improvements:

- The theoretical capacity would increase to 255 mAh/g.
- The voltage over two-thirds of the capacity range would rise to above 4V.

An obvious consequence of this is that the upper-voltage plateaus (>4V) could be exploited in EV applications, despite the fact that the undoped LFS material is only at 2.8V vs. Li/Li$^+$.

An important note: Even unsubstituted LFS can be exploited to huge advantage in lower-voltage (2.8V) large-scale Li-ion batteries for sustainable energy storage; this stored electrical energy can, in turn, be used to charge EV batteries.

The scientific challenge here has been to better understand the crystal chemistry of this family of materials so that the structural/chemical conditions around the TM-ions in the LFS structure can be optimized to promote a reversible $>\pm1$ change in the TM-ion oxidation-state. We have made great progress in this endeavor, even if the ultimate breakthrough has not yet materialized, at least not from our own research – but perhaps elsewhere. Our GCEP project has been hugely catalytic in provoking international interest in LFS. Most groups around the World who research into new cathodes for Li-ion batteries now have LFS-related materials on their agenda. Something very significant for the future of electrical energy storage will surely emerge soon.

Background

Despite what is often depicted today as the failure of the Copenhagen Climate Summit of December 2009, a great deal is happening worldwide in the car industry with a focus on the development of low- or zero-fuel vehicles. Indeed, EV-related research groups and companies now exist in virtually every industrial nation on the planet. The present situation can be summarized in the rhetorical question posed in the advertisement for the SAE International Battery Vehicle Summit held in Shanghai, September 2010:
“Lithium-ion battery technology for use in hybrid, plug-in hybrid and electric vehicles is maturing and will play a key role in electric vehicle development and sales. But how quickly is this technology progressing, and perhaps more importantly, what battery designs will guarantee reliability and safety while providing the best balance of cost and performance?”

It would therefore be tempting to conclude that we have already turned the corner in making the transition from a fossil fuel- to an electricity-based transport system, especially in the small-car sector. Any car producer who is to survive the latest economic crisis must move seriously towards the development of HEV/Plug-In HEV/EV concepts for the World market. However, the optimal battery (realistically, of a Li-ion type for at least the next generation) has yet to emerge to drive this development forward. What is more, the one factor 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**: An on-board auxiliary battery in some form of hybrid concept could soon become a standard option in all cars sold. It made its market entry in the Toyota PRIUS in November 1997.

- **Plug-in HEVs**: These can use overnight (off-peak) grid power to charge what must be a considerably larger battery than that in an HEV. A battery serves as the sole power source during the first miles of a trip, until the HEV-mode cuts in at the EV-to-HEV threshold point. The latest Toyota PRIUS is of this type; it is now moving into wide-scale production despite the fact that this cut-in threshold to HEV-mode occurs at only an unimpressive 30-50 km.

- **Pure EVs**: These are “pure electric”, using no other backup motor. This type of vehicle is obviously to be preferred from a GHG-emissions viewpoint, but places greater demands on battery performance and safety, since there need much larger battery-packs. There are today a number of Chinese companies claiming to produce Li-ion batteries for EV applications, but their long-term life and safety are still unproven.

The current status in cathode development for up-scaled Li-ion batteries can be summarized:

- **Capacities must be doubled** – to reach ca. 300 Ah/kg; this was the ultimate goal of this project through our seeking to find an ideal “≥1 el. reaction” system. Although this has not been achieved within our Uppsala GCEP project, there are already indications that these breakthroughs are on their way.

- Cost limitations in large-scale batteries imply that Fe and Mn are realistically the only TM candidates. As regards specific materials: LFP has its limitations, related to there only being 1 Li per TM atom per formula unit, while the layered $LiNi_{x}Mn_{y}Co_{z}O_{2}$ materials will have a cost problem. Nickel is also an environmental hazard in larger quantities. A >1 electron reaction is a rational low-cost solution.

- **Lower-cost large-scale synthesis methods** must be found. Hydrothermal synthesis is the current favorite, but a continuous production technology must be developed to cope with the volumes anticipated in the coming market. Some alternative synthesis technique may be necessary.

**Conclusion**: Li-Fe-silicates have a bright future in large-battery applications!
Results

Our general approach has throughout involved a selective Density Function Theory (DFT) based computer-screening procedure, followed by the use of a range of synthetic and characterization techniques (electrochemical cycling, \textit{in situ} powder XRD and ND, SEM and HR-TEM microscopy, \textit{in situ} Mössbauer and XPS/PES spectroscopies, particle-size and electrode porosity measurements, ...) to pinpoint the precise structural and chemical conditions necessary to promote a reversible $\Delta > +/-1$ change in oxidation-state in an electrochemically active TM-ion. The year-by-year strategy which we followed during the project is summarized in Fig. 1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{A summary of the general strategy and methodology used in: (a) Years 1 and 2; and (b) Year 3 of the project.}
\label{fig:figure1}
\end{figure}

1. DFT-based materials design

Our earlier DFT calculations [1,2] exploited three types of structural modification (as summarized in Fig. 2.); each has had its own special role to play in the materials-design strategy to meet the challenges we have identified to improve the electrochemical performance of LFS:

A: Non-stoichiometry - for capacity enhancement.
B: TM-substitution - for capacity enhancement and structural stabilization.
C: Polyanion substitution - for electronic conductivity enhancement.
These three types of modification have been the prime focus of our design strategy in the project.

**Figure 2:** A schematic of the materials design strategies exploited in the project to enhance the performance (esp. capacity and rate) of Li$_2$FeSiO$_4$ as a Li-ion battery cathode material.

**Charge transport in Li$_2$FeSiO$_4$**

Earlier work has shown that mixing of the Li- and Fe-site occupations is an important structural feature in determining the electrochemical properties of LFS [3]. Preferred Li$^+$ ion diffusion pathways and activation barriers for migration have thus been estimated from DFT calculations for both the un-mixed (SG Pmn2$_1$) and mixed (β-Li$_2$CoSiO$_4$ structure: SG Pbn2$_1$) models for LFS [4]. This latter structure corresponds to the situation where 100% of the Fe and Li site-occupations are reversed; see Fig. 3. In both models, the Li$^+$ diffusion is two-dimensional, but the activation barriers are ca. twice higher as in other cathode materials like LiCoO$_2$ and LFP - explaining the higher polarization on low-temperature cycling of LFS. An obvious implication is that deintercalation kinetics could be improved if we can create preferentially rod-like particles with the diffusion plane perpendicular to the rod axis.
Figure 3: Li\(^+\) migration pathways with corresponding energy profiles calculated for “un-mixed” (a) and “mixed” (b) Li/Fe-site models for the Li\(_2\)FeSiO\(_4\) structure.

DFT calculation were also used to estimate the electronic conductivity which, in these materials, is achieved by a polaron mechanism, i.e., by switching valence between Fe\(^{2+}\) and Fe\(^{3+}\); see Fig. 4.

![Figure 4: Electron transfer between Fe\(^{2+}\) and Fe\(^{3+}\) according to Marcus theory [5] is shown schematically for Li\(_2\)FeSiO\(_4\) (left). The calculated activation energies \(E_a\) and polaron jump distances are shown in the Table (right), together with data reported for LiFePO\(_4\).](image)

<table>
<thead>
<tr>
<th>Model</th>
<th>Jump distance</th>
<th>(E_a)/eV</th>
</tr>
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<tbody>
<tr>
<td>Li(_2)FeSiO(_4) Pmn(<em>2)</em>(_1)</td>
<td>4.43</td>
<td>0.23</td>
</tr>
<tr>
<td>Li(_2)FeSiO(_4) Pbn(<em>2)</em>(_1)</td>
<td>4.45</td>
<td>0.22</td>
</tr>
<tr>
<td>Li(_2)FeSiO(_4) Pbn(<em>2)</em>(_1)</td>
<td>5.11</td>
<td>0.24</td>
</tr>
<tr>
<td>LiFePO(_4)</td>
<td>(3.96)</td>
<td>0.215</td>
</tr>
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</table>

The electron hopping rate in LFS is low, due mainly to longer Fe-Fe distances which weaken the electronic coupling \(V_{AB}\). This issue has here been addressed by incorporating excess TM-ions to create a non-stoichiometric structure, or by substituting the SiO\(_4\)\(^4-\) polyanions, e.g., by VO\(_4\)\(^3-\) ions. However, our calculations [6] suggest that such substitution increases the activation energy by \(~0.3\)eV. A balance must clearly be found between the various possible substitution strategies.

Stabilization of the Li\(_2\)MnSiO\(_4\) structure

Since the structure of Li\(_2\)MnSiO\(_4\) (SG Pmn\(_2\)_\(_1\)) is now widely known to be unstable on deep delithiation [7-11], the substitution of electrochemically inactive ions (so-called “bystander” ions) into the Mn- and Si-sites has been investigated extensively with the general goal of stabilizing the structural degradation during a potential >1 electron redox reaction; see Fig. 5.
Figure 5: A 50% Mg-substitution of Mn in the Li₂MnSiO₄ (SG Pmn2₁) structure; the Mg bystander-ion is circled (left). A calculated delithiation voltage of 4.4V is found for the Mn²⁺ ↔ Mn⁴⁺ transition in this system on the right, with the distorted Mn⁴⁺ coordination tetrahedron highlighted (red circle).

Our calculations suggest that, even for 50% substitution of the Mn-site by different bystander ions (Mg, Ni, Zn, Cu, Ca, ...), none is able to suppress the distortion found earlier in the Mn-coordination tetrahedra [2]. We are therefore now tempted to suggest that precisely this distortion may prove to be a necessary structural condition for successful “>1 electron reaction” cycling. Recent unpublished experimental results (not our own) suggest that this can actually be the case in the Mg²⁺ bystander-ion system Li(Mn,Mg)PO₄. In fact, these types of substituted material tend to crystallize in polymorphs with inverse Li/Mn site-occupations [12], which generally undergo less structural rearrangement on cycling.

Other related materials
(a) Earlier calculations for the lithiated and delithiated Fe- and Mn-counterparts of Na₂Mn₂Si₂O₇ are exemplified in Fig. 6. The higher packing density of cations in pyrosilicates makes them a very attractive “upgrade” from the well known pyrophosphate counterpart LiFeP₂O₇ [13]. Moreover, disilicate structures provide a continuous network of M-O-M connectivity, facilitating higher electron transfer rates compared to those in the pyrophosphates. Delithiation at 3.1V for the Fe- and at 3.7V for the Mn-systems to provide ca. 180mAh/g give reason for optimism, since the theoretical capacity for LiFeP₂O₇ is only 113 mAh/g at ca. 2.9V.

Figure 6: The structures of Na₂Mn₂Si₂O₇-based Li₂Fe₂Si₂O₇ (left) and delithiated Fe₂Si₂O₇ (right) derived from DFT calculations: Li(yellow); FeO₆(green); SiO₄(blue).
Since our efforts to synthesize Li$_2$Mn$_2$Si$_2$O$_7$ gave impurities of type Mn$_2$SiO$_4$, Li$_2$MnSiO$_4$, Li$_2$SiO$_3$ and SiO$_2$, formation energies were calculated to estimate the phase stability of A$_2$M$_2$Si$_2$O$_7$ (A=Li, Na; M=Fe, Mn) compared to the impurity phases (Table I). The results suggest that only the Na-form is thermodynamically stable, implying that a two-step synthesis for Na$_2$Mn$_2$Si$_2$O$_7$, followed by ion-exchange, could be rewarding – but still no significant breakthroughs to report on this front!

**Table I.** Calculated formation energies for A$_2$M$_2$Si$_2$O$_7$, A=Li, Na; M=Fe, Mn.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{\text{form}}$/eV per f.u.</th>
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<tbody>
<tr>
<td>Li$_2$MSiO$_4$ + 0.5(M$_2$SiO$_4$ + SiO$_2$) = Li$_2$M$_2$Si$_2$O$_7$</td>
<td>0.52 (Fe)</td>
</tr>
<tr>
<td></td>
<td>0.61 (Mn)</td>
</tr>
<tr>
<td>M$_2$SiO$_4$ + Li$_2$SiO$_3$ = Li$_2$M$_2$Si$_2$O$_7$</td>
<td>0.39 (Fe)</td>
</tr>
<tr>
<td></td>
<td>0.58 (Mn)</td>
</tr>
<tr>
<td>M$_2$SiO$_4$ + Na$_2$SiO$_3$ = Na$_2$M$_2$Si$_2$O$_7$</td>
<td>-0.01 (Mn)</td>
</tr>
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</table>

(b) Calculations have also probed the SiS$_4^{4-}$-derivative of Li$_2$MSiO$_4$ [14]. An anion lattice of S-ions would raise the valence-band with respect to the more stable oxygen lattice, leading to improved electron transfer and therefore better kinetics at lower temperatures. Earlier DFT calculations show that delithiation occurs at ca. 3.0V for the Fe-material, and at a low 3.3V for its Mn-counterpart; the calculated band-gap was reduced by ca. 2eV. New calculations of the Mn-system, however, suggest that the 4-fold coordination of the Mn in the completely delithiated structure becomes unstable, indicating structural irreversibility in an electrode material. We have therefore not followed this up with any corresponding experimental work on SiS$_4^{4-}$-anion systems.

2. Advances in synthesis

A wide range of techniques have been used in the course of the project to synthesize LFS-related materials. Some features worthy of mention are:

(a) **Solid-state synthesis** is highly sensitive to the nature of the reducing gas and amount of carbon-additive used [15,16,17].

(b) **Hydrothermal synthesis** has produced LFS with a first-cycle capacity of 160mAh/g, and stable cycling at ca. 140 mAh/g and C/20 rate – even under sub-optimal conditions. Particle-sizes were ca. 100 nm.

(c) A **solvothermally-assisted sol-gel process** has also been used with considerable success. Smaller particle-sizes, lower levels of impurity – and improved battery performance - have been achieved; as illustrated in Fig. 7. Interestingly, following the lead given by DFT modeling of diffusion (above) that control of particle-shape (to encourage particle elongation) could result in improved electrochemical performance, it was actually found that varying the synthesis conditions could indeed result in elongated LFS particles (Fig. 8).
Figure 7: Cycling curves, capacities, morphology and rate performance (top-left to bottom-right) obtained for Li$_2$FeSiO$_4$ synthesized by the solvothermally-assisted sol-gel technique.

Figure 8: SEM image of the rod-shaped Li$_2$FeSiO$_4$ nanoparticles. The inset is a TEM image of a particle with a diameter of only 30nm.

(d) Microwave-assisted synthesis [18,19] has given encouraging results, especially considering the greatly shortened synthesis times (Fig. 9); this is critical for any viable large-scale industrial process.
Figure 9: The dramatically shortened synthesis times realized by microwave-assisted synthesis (left), and the resulting rate performance of the resulting Li$_2$FeSiO$_4$ material (right) for process times in the minutes range, cf. our first successful solid-state syntheses took 2-3 months with only marginally better results.

3. Examples of the Li$_2$FeSiO$_4$-related cathode materials studied

(a) Mn-substitution into LFS

![Voltage Profile](image1)

![Cycling Performance](image2)

Figure 10: Voltage cycling profile (a) and capacity (b) at 60°C of bulk Li$_2$Mn$_{0.1}$Fe$_{0.9}$SiO$_4$.

The substitution of 10% Mn into LFS to give Li$_2$Mn$_{0.1}$Fe$_{0.9}$SiO$_4$ should facilitate the extraction of additional lithium, corresponding to the activation of the redox reactions Mn$^{2+}$$\leftrightarrow$Mn$^{3+}$$\leftrightarrow$Mn$^{4+}$. The material was prepared by traditional solid-state methods to give particle sizes in the region of 200nm (Figure 10). This material was cycled over the range 2-4.2V. A small plateau occurs at ~4V corresponding to the Mn$^{3+}$ oxidation state during the first cycle, but disappeared on subsequent cycling. The 1$^{st}$ and 2$^{nd}$ charge capacities were 161 and 177 mAh/g, while the discharge capacities are constant at ~45mAh/g, suggesting that the Li$_2$Mn$_{0.1}$Fe$_{0.9}$SiO$_4$ material does not cycle reversibly. Though small improvements could be made to this early result, the problem of cycling the Mn-substituted material remain unsolved - worldwide.

(b) The non-stoichiometric system: Li$_{2-2x}$M$_{1+x}$SiO$_4$, M=Fe, Mn, Co

Initial DFT calculations indicated that it should be possible to extract up to 1.25 Li (~200 mAh/g) from the non-stoichiometric compound (Li$_{1.5}$Fe$_{1.25}$SiO$_4$) without destabilizing its Li$_3$PO$_4$ type structure. The material was synthesized by heating its precursor, prepared using the citrate-based polymerization method. Electrochemical cycling of unoptimized test-cells (0.8M LiBOB in 2:1 EC:DEC) using this as cathode material showed good reversible cyclability, with an
average charge/discharge capacity of ~105 mAh/g (not correct for carbon black (CB) content), and with voltage profiles similar to those of bulk LFS; Figure 11. Our hopes were raised!

Figure 11: Cycling profiles (left) and capacity (right) for the first 10 cycles of Li$_{1.8}$Fe$_{1.25}$SiO$_4$ (cycling temperature: 60 deg. C); note the 1$^{\text{st}}$ cycle anomaly (red curve).

Unfortunately, further work on this system has been held back by the discovery (from XRD studies) that these materials were “2-phase”: normal LFS in coexistence with a still undefined electrochemically active amorphous phase. This same frustrating phenomenon has reappeared for other compositions within this non-stoichiometric family of LFS materials; no solution has yet been found.

(c) The bystander-ion system Li$_2$Mn$_{0.5}$Mg$_{0.5}$SiO$_4$ has been found to crystallize in the Li$_2$MgSiO$_4$ structure (SG: P2$_1$/n), which is the same structure as the electrochemically active HT phase of Li$_2$MnSiO$_4$ [12]; see Fig. 12. We are now endeavoring to show that this Li$_2$Mn$_{0.5}$Mg$_{0.5}$SiO$_4$ material is also an electrochemically active phase but is formed at a ~500 °C lower temperature, as a result of the use of the Mg bystander-ion substitution. Preliminary cycling results are promising. This can perhaps be the seed to the breakthrough we are looking for.

Figure 12: XRD powder profiles for Li$_2$MnSiO$_4$ and Li$_2$Mn$_{0.5}$Mg$_{0.5}$SiO$_4$.

(d) Pyrosilicates involving Si$_2$O$_7$ entities could well be more stable due to the shorter bridging between the TM-ions; this should also improve electrochemical efficiency through better electronic conductivity and more efficient electron transfer at the interface. Solid-state and
hydrothermal synthesis routes were used to make \( \text{Li}_2\text{Mn}_2\text{Si}_2\text{O}_7 \) – but both routes failed. Confirming earlier prediction from DFT calculations (above) that only the Na-counterpart is thermodynamically stable, this Na-version of the material was made successfully. The results are shown in Fig. 13.

![Figure 13: XRD patterns (left) of \( \text{Na}_2\text{Mn}_2\text{Si}_2\text{O}_7 \) synthesized with shorter (top) and longer (middle) process times compared to the reference material (bottom); an SEM image (middle) shows elongated particles (right).](image)

Finally, it was noted that careful pre-cycling of the \( \text{Li}_2\text{MnSiO}_4 \) system by successively raising the upper cut-off voltage from 3.7 to 4.2 to 4.4 V stabilized the cycling - between two still unidentified phases (Fig. 14). This is a remarkable result in the light of earlier reports of rather unimpressive cycling behavior for pure \( \text{Li}_2\text{MnSiO}_4 \); but note the handicappingly large (ca. 1.5 V) polarization.

![Figure 14: Quasi-stable cycling of pure \( \text{Li}_2\text{MnSiO}_4 \)](image)

4. Safety/stability issues
Safety issues are intimately related to the formation and behavior of the SEI layer on the composite electrodes in the battery during cycling. A much improved understanding of this surface-film formation on LFS cathodes was achieved for a wide range of different electrolyte/salt systems using a careful (already classic) X-Ray Photoelectron Spectroscopy (XPS) study; see Fig. 15.
A systematic study was also made of the effects of cell-cycling - after 50 cycles at 50°C using 1M LiX 2:1 EC:DEC electrolytes, where the salt (LiX) was LiPF$_6$, LiBOB, LiTFSI, LiTDI and LiPDI; the latter two salts are new; see [20]. Some general conclusions could be drawn:

- **LiPF$_6$**: A dynamic SEI layer with a range of degradation compounds dependent on state-of-charge: indications of salt degradation (LiF) and small amounts of carbon-based reaction products.
- **LiTFSI**: An electrochemically stable salt giving good surface-layer coverage with few salt-based species; some decomposition of solvent species.
- **LiBOB**: An electrochemically stable salt - with no significant surface-layer formation; some indication of polymeric decomposition products from the EC/DEC solvent.
- **LiTDI/LiPDI** (the new salts tested): A dynamic and possibly reversible SEI layer was formed, giving excellent and consistent electrochemical performance; the dynamic changes observed were state-of-charge (SOC) dependent.

**To summarize**: We could provide convincing evidence of the intrinsic high stability of an LFS cathode – at least equal to that of LFP. This (along with cost) is arguably the most attractive feature of LFS in terms of its relevance to up-scaled Li-ion battery applications, in combination with its potential for hosting a >1 electron reaction.

5. The performance of Li$_2$FeSiO$_4$ positive electrodes in “whole-cell” batteries.

A single dominant issue emerged around the middle of the project: it became urgent to address the critical question of the cyclability of an LFS positive electrode vs. a graphite negative electrode - in so-called “whole-cells”. Difficulties were experienced in getting such “whole-cells” to cycle with any measurable capacity. If LFS is not able to function in conjunction with a graphite negative electrode, its future as a Li-ion battery cathode material is seriously threatened; graphite is the material of choice in virtually all of today’s commercial Li-ion battery concepts. For this reason, the decision was taken to prioritize this issue above all others with the
motivation that the problem could actually be intrinsic to the LFS system. An extensive survey of the cycling performance of whole-cells using a 3-electrode system for five different Li-salts (LiTFSI, LiBOB, LiPF₆, LiTDI and LiPDI) in the temperature range 25 - 60°C concluded that, although LFS cycled well in half-cells using conventional electrolytes, problems most certainly arose on cycling LFS against graphite negative electrodes. This is well illustrated in Fig. 16, which shows the cycling of a half- and whole-cell at 60°C; there is no reversible capacity available from the whole-cell.

![Figure 16](image)

**Figure 16:** The potential profile of Li₂FeSiO₄ cycled at 60°C against metallic lithium (left) and graphite (right).

Systematic studies have been made using a number of “3-electrode whole-cells” and a variety of electrolytes and counter-electrodes, and cycling at different temperatures ranging from 25 to 60°C, where the function of the anode and the cathode can be followed independently (Fig. 17).

![Figure 17](image)

**Figure 17:** Charging curves for 3-electrode cells of Li₂FeSiO₄ vs. graphite; electrolyte – EC:DEC 1M LiPF₆; red: Li₂FeSiO₄; green: graphite; blue: whole-cell voltage; purple: graphite vs. Li/Li⁺ in half-cell.

Happily, it has been shown that the problem lies (as it did in early work with LFP) on the graphite electrode side, and is not intrinsic to the LFS material. Careful cell-balancing has subsequently been able to give a well-cycling whole-cell after optimizing cycling temperature vs. electrolyte (esp. salt type). The graphite electrode functions well at temperatures close to room temperature, while LFS functions well at 60°C; as a compromise, we chose to cycle our 80mAh demonstration whole-cell at 40°C; see Fig. 18.
We believe this is the first whole-cell demonstrator which exploits an LFS cathode. Though far from fully optimized, these demo-cells give great promise for the future. Skilled battery engineers can readily tune the system to cycle with optimal capacity. A number of future directions for further development in this more practical aspect of the work readily suggest themselves:
- Development of a more stable electrolyte exploiting custom-designed additives.
- Further reduction of particle-size down to 20-30 nm – to improve cycling performance.
- Development of appropriate coatings.

Li$_2$FeSiO$_4$-based Li-ion batteries retain their attraction; they are now being studied in most countries engaged in Li-ion battery research.

![Graph](image1.png)

(a) ![Graph](image2.png)

(b) ![Graph](image3.png)

(c) ![Graph](image4.png)

(d)

**Figure 18:** A “successful” voltage cycling profile (a) for a prismatic 80 mAh demonstration whole-cell (b) with an Li$_2$FeSiO$_4$ cathode and a balanced graphite anode. Charge and discharge capacities (c and d) for a 4-cell test pack at constant current and 40°C.

**Conclusions:**
- This GCEP project has unquestionably been catalytic in provoking huge international interest in LFS. LFS is today the major focus of interest in many Li-ion battery material research laboratories worldwide.
- Our original publication on LFS has become the most cited paper in *Electrochemical Communications* during the 5-year period 2005-2010.
- LFS has been shown to work satisfactorily in demo “whole-cell” Li-ion batteries vs. a graphite anode.
LFS can be synthesized both quickly (in < 1 h), cheaply (using low-cost raw materials), cleanly, and at low energy cost.

LFS is probably the safest cathode material available today – a critical feature for EV and sustainable energy storage applications.

LFS today finds itself in an almost identical situation to that of LFP ten years ago; LFP is today seen as the cathode-of-choice for large-scale EV applications, while LFS has several potential advantages over LFP: safer, “greener”, higher storage capacity and even higher voltage vs. Li/Li+ when appropriately modified.

The clue to where the key performance breakthrough lies for LFS and related systems can come from the LFP system itself: a complete LiMn\(_{1-x}\)Mg\(_x\)PO\(_4\) solid solution has recently been made (unpublished work); it could be shown that and the Mg\(^{2+}\) bystander-ion gave a 0.2V increase in the Mn\(^{2+}/\)Mn\(^{3+}\) redox potential. More spectacular, however, was the activation of the Mn\(^{2+}/\)Mn\(^{3+}\) redox couple at 4.8 V via this Mg\(^{2+}\) substitution. We are now optimistic that by-stander ion substitution (typically: by Mg\(^{2+}\) in Li\(_2\)Mn\(_0.5\)Mg\(_0.5\)SiO\(_4\)) can trigger the “quantum leap” in cathode capacity implied in our project title.

**Publications 2008-2010:**


Also:

International conference presentations: 2008-2010

At: American Automotive Battery Conference (AABC), Tampa, Florida, May 2008:
- 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. (poster)

At: International Meeting on Lithium Batteries (IMLB2008), Tianjin, China, June 2008:
- Strategies for optimizing the performance of silicate-based cathodes for Li-ion battery applications, Kam, K., Liivat, A., Gustafsson, T. and Thomas, J.O. (talk)

At: International Meeting on Lithium Batteries (IMLB2008), Tianjin, China, June 2008:
- Modelling non-stoichiometry and disorder in silicate-based cathode materials, Liivat, A., Larsson, P. and Thomas, J.O. (poster)

At: International Meeting on Lithium Batteries (IMLB2008), Tianjin, China, June 2008:
- Modelling the surface layer on Li2FeSiO4 from systematic XPS analysis, Stjerndahl, M., Ensling, D., Gustafsson, T. and Thomas, J.O. (talk)

At: 49th Battery Symposium in Japan, Sakai, Osaka, November 2008:
- Optimizing the performance of iron silicate based cathodes for upscaled Li-ion battery applications, Thomas, J.O. (invited talk)

At: International IUPAC Conference, Glasgow, Scotland, 2-7 August 2009:
- A silicate-based cathode material for lithium-ion batteries, Kam, K.C., Liivat A. and Thomas, J.O. (talk)

At: Lithium Battery Discussion on Electrode Materials, Arcachon, France, 20-25 September 2009:
- How do the silicates fit in? J. O. Thomas. (invited talk)
- The Li-ion extraction/re-insertion mechanism in Li2FeSiO4. Armstrong, A.R., Bruce, P.G., Gustafsson, T. and Thomas, J.O. (poster)
- Combined SXPS and SXAS study of the electrochemical intercalation reaction of Li2NiTiO4 Cathodes. Ensling, D., Kuezma, M., Dominko, R., Gustafsson, T., Thomas, J.O. and Gaberscek, M. (poster)
- Surface-film formation on Li2FeSiO4 cathodes for different electrolyte systems studies by XPS. Ensling, D., Jiang, Y., Gustafsson, T. and Thomas, J.O. (poster)
At: The 216th ECS Meeting, Vienna, Austria, October 4-9, 2009:
- Enhanced Capacity from Non-stoichiometric Lithium Iron Silicate, Li_{2-x}Fe_{1+x}SiO_4,
  Kam, K.C., Liivat, A., Ensling, D., Gustafsson, T. and Thomas, J.O. (talk)
- A new cathode material for Li-ion batteries with the possibility of extracting two Li-ions per
  and Gaberscek, M. (talk)

At: The 4th International Forum of the Technology of Li-Ion batteries, Beijing; 16-18 Oct. 2009:
- (How) can iron silicates compete with the phosphates? Thomas, J.O. (invited talk)

At: The 50th Japanese Battery Symposium, Kyoto; 30 Nov. - 2 Dec. 2009:
- New directions in up-scaled Li-ion battery cathodes. Kam, K.C., Liivat, A., Gustafsson and
  Thomas, J.O. (invited talk)

At: The International Meeting on Lithium Batteries (IMLB-15), 27 June-2 July 2010, Montreal, Canada:
- Polyanion substitution into silicate-based cathode materials. Liivat, A. and Thomas, J.O. (Poster)
- Inexpensive synthesis of Li_{2}FeSiO_{4} for up-scaled LIB cathodes. Tan, S., Kam, K.C.,
  Thomas, J.O. and Gustafsson, T. (talk)

References
[1] Larsson, P., Ahuja, R., Nytén, A., Thomas, J. O., An ab initio study of the Li-ion battery cathode material
  Li_{2}FeSiO_{4}. Electrochem. Commun., 8, 797-800 (2006)
[2] Larsson, P., Ahuja, R., Liivat, A., Thomas, J. O., Structural and electrochemical aspects of Mn substitution
  into Li_{2}FeSiO_{4} from DFT calculations, Comp. Mater. Sci., 47, 678-684 (2010)
[6] Liivat, A., Thomas, J.O., A DFT study of VO_{4}^{3-} polyanion substitution into the Li-ion battery cathode
  material Li_{2}FeSiO_{4}. Comp. Mater. Sci., 50 (2010) 191
[7] Dominko, R., Bele, M., Kokalj, A., Gaberscek, M., Jamnik, J., Li_{2}MnSiO_{4} as a potential Li-battery cathode
  material, J. Power Sources, 174, 457-461 (2007)
[8] Li, Y.-X., Gong, Z.-L., Yang, Y., Synthesis and characterization of Li_{2}MnSiO_{4}/C nanocomposite cathode
  material for lithium ion batteries, J. Power Sources, 174, 528-532 (2007)
[9] Belharouak, I., Abouimrane, A., Amine, K., Structural and Electrochemical Characterization of Li_{2}MnSiO_{4}
[10] Deng, C., Zhang, S., Yang, S., Effect of Mn substitution on the structural, morphological and
  electrochemical behaviors of Li_{2}Fe_{1-x}Mn_{x}SiO_{4} synthesized via citric acid assisted sol-gel method,
[11] Liu, W., Xu, Y., Yang, R., Synthesis, characterization and electrochemical performance of Li_{2}MnSiO_{4}/C
  cathode material by solid-state reaction, J. Alloys Comprd., 480, L1-L4 (2009)
  Crystal structure, phase relations and electrochemical properties of monoclinic Li_{2}MnSiO_{4},
[15] Li, L., Guo, H., Li, X., Wang, Z., Peng, W., Xiang, K., Cao, X., Effects of roasting temperature and
  modification on properties of Li_{2}FeSiO_{4}/C cathode, J. Power Sources, 189, 45-50 (2009)
[16] Kam, K.C., Gustafsson, T., Thomas, J.O., Synthesis and electrochemical properties of nano-structured
  Li_{2}FeSiO_{4}/C cathode materials for Li-ion batteries. Solid State Ionics (2010),
  doi:10.1016/j.ssi.2010.03.030 (volume seriously delayed)
  synthesis of the Li-ion battery cathode material Li_{2}FeSiO_{4}. Submitted to: Electrochemical and Solid-State
  Letts.
[18] Guo-Rong, H., Yan-Bing, C., Zhong-Dong, P., Ke, D., Qing-Lai, J., Preparation of Li_{2}FeSiO_{4} Cathode
  (2009)
  Li_{2}FeSiO_{4}.

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