

A Quantum Leap Forward for Li-Ion Battery Cathodes

GCEP Technical Report 2010 (Year 3)

Investigators

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Abstract

Our 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 prime goal to extract >1 electron per 3d-metal, and thereby achieve a cathode material capacity ultimately well in excess 200 mAh/g. We exploit a DFT-modeling based screening procedure – followed by efforts to synthesize what are seen as the most promising candidate materials. Earlier theoretical screening work had suggested three general strategies:

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

New theoretical results included Li-ion diffusion calculations for “un-mixed” and “mixed” Li/Fe-ion systems, which show Li^+ diffusion to be two-dimensional in the $\text{Li}_2\text{FeSiO}_4$ structure, suggesting that Li-insertion/de-insertion kinetics (and hence cathode performance) can be improved if the growth of rod-like particles can be promoted with their diffusion plane perpendicular to the rod axis. This is being tested experimentally. It has also been found that TM-ions can be incorporated into the non-stoichiometric structure, $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$, to give shorter TM-TM ion distances, higher electron-hopping rates - and hence higher electronic conductivities. Surprisingly, even 50% substitution of the Mn-site in $\text{Li}_2\text{MnSiO}_4$ 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 tetrahedral. Finally; 12.5% substitution of VO_4^{3-} into the SiO_4 site in $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{CoSiO}_4$ results in increased capacity and electronic conductivity.

Synthetic techniques have been exploited further: *hydrothermal synthesis* is now able to give first-cycle capacity as high as 160mAh/g in $\text{Li}_2\text{FeSiO}_4$, with stable cycling at *ca.* 140 mAh/g and C/20 rate – even under sub-optimal conditions. A *solvothermally-assisted sol-gel process* has also been used with considerable success to control particle-shape. It was noted earlier that improved performance should result from a predominance of elongated particles. The *solid-state synthesis* of $\text{Li}_2\text{FeSiO}_4$ was also found to be highly sensitive to the type of reducing gas and amount of carbon-additive used. *Microwave-assisted synthesis* has also shown dramatically fore-shortened synthesis times: from days to minutes.

Our *experimental* work has shown that:

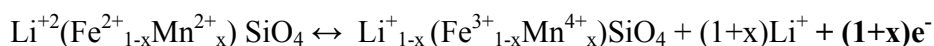
- The *bystander-ion* system $\text{Li}_2\text{Mn}_{0.5}\text{Mg}_{0.5}\text{SiO}_4$ crystallizes in the $\text{Li}_2\text{MgSiO}_4$ structure (SG: $\text{P2}_1/\text{n}$). We are now hoping to show that this material is electrochemically active, though formed at a ~ 500 °C lower temperature, as a result of the introduction of the bystander-ion Mg.
- The *non-stoichiometric* system $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$, $x=0.25$ shows first-cycle capacity of ~ 200 mAh/g, but we are still unable to make an unequivocal determination of structure and phase purity (due largely to the poor quality of the XRD data). Better quality neutron diffraction (ND) data has now been obtained, and is now being used in combination with the results from *Mössbauer spectroscopy* in an intense effort to finally solve the non-stoichiometric structure.
- Solid-state and hydrothermal synthesis routes have been used in an attempt to obtain the *pyrosilicate* system $\text{Li}_2\text{Mn}_2\text{Si}_2\text{O}_7$ – in which we can expect to encounter much shorter Mn-Mn distances. It is found, however, that only its Na-counterpart is thermodynamically stable; suggesting that a two-step synthesis *via* $\text{Na}_2\text{Mn}_2\text{Si}_2\text{O}_7$, followed by Li^+ ion-exchange, must be used instead.
- Extensive XPS studies have provided further convincing evidence for the *intrinsically high chemical and electrochemical stability* of the $\text{Li}_2\text{FeSiO}_4$ cathode system – at least equal to that of LiFePO_4 . 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 $\text{Li}_2\text{MnSiO}_4$ system by successively raising the upper cut-off voltage from 3.7 to 4.2 to 4.4 V 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.
- 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 a $\text{Li}_2\text{FeSiO}_4$ cathode and a graphite anode.

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 or continued optimism, a totally sustainable solution could (if we are realistic) take the better part of the 21st Century to achieve. We must be aware that progress in the Battery World has always been notoriously slow. We have now 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 “ >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 LiFePO_4 . 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 $\text{Li}_2\text{FeSiO}_4$, 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 $\text{X}^{2+} \leftrightarrow \text{X}^{3+} \leftrightarrow \text{X}^{4+}$ 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:



This is shown schematically in *Fig. 1*, which depicts the charging curve for the case of 50% Mn-substitution of $\text{Li}_2\text{FeSiO}_4$, *i.e.*, $x = 0.5$. This would have three important effects:

- The theoretical capacity would increase to 255 mAh/g.
- The voltage over two-thirds of the capacity range (the upper RED plateaus) would rise to above 4V.
- The entire upper-voltage plateaus ($>4\text{V}$) could be exploited in EV applications, despite the facts that the undoped cathode material is only *ca.* 2.8V vs. Li/Li^+ .

Note: Even the “unsubstituted” green curve can be exploited to advantage in lower-voltage (2.8V) large-scale Li-ion batteries for sustainable energy storage; the stored electrical energy can, in turn, be used to charge EV batteries of some other type.

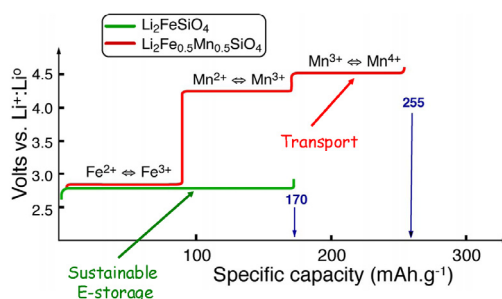


Figure 1: A schematic representation of the capacity gains to be achieved by replacing 50% of the Fe in $\text{Li}_2\text{FeSiO}_4$ by Mn.

The scientific challenge here is then to better understand the crystal chemistry of this family of materials so that the structural/chemical conditions around the TM-ions in the $\text{Li}_2\text{FeSiO}_4$ structure can be optimized to promote a reversible $>\pm 1$ change in the TM-ion oxidation-state.

Background

Despite the apparent failure of the *Copenhagen Climate Summit* of December 2009, a great deal is happening today 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 recent advert for the coming *SAE International Battery Vehicle Summit* to be held in Shanghai, Sept. 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 drive 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 transition from a fossil-fuel based to an electricity-based transport system, especially in the small-car sector. Any car producer who is to survive the on-going 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 the Li-ion type) *has yet to emerge to drive this development forward*, and 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. The latest Toyota PRIUS is of this type; it is now moving into wide-scale production despite the fact that the cut-in threshold to HEV-mode occurs at only a meagre *ca.* 20 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 point of view, but places the greatest demands on battery performance and safety. There are several Chinese companies claiming to produce Li-ion batteries for EV applications, but their intrinsic safety is still in question.

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 is the ultimate goal of this project through our seeking to find an ideal >1 el. reaction system.
- Cost limitations in large-scale batteries imply that *Fe* and *Mn* are realistically the only TM candidates. As regards specific materials: *LiFePO₄* has its limitations, related to there only being 1 Li per TM atom per formula unit, while the layered *LiNi_xMn_yCo_zO₂* 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 continuous production-lines must be developed to cope with the volumes anticipated in the coming market.

There are clear applications for the Li-Fe-silicates!

Results

Our general approach has continued to involve selective Density Function Theory (DFT) based computer-screening procedures, followed by the 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 try to discover 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 followed in the project is summarized in *Fig. 2*.

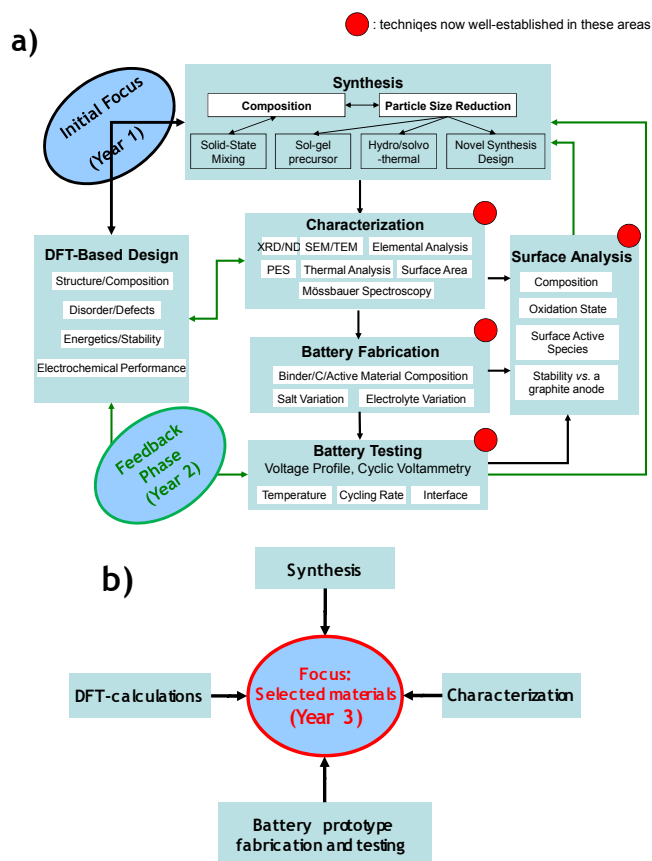


Figure 2: A summary of the general strategy and methodology used in: (a) *Years 1 and 2*: and (b) *Year 3* of the project.

1. DFT-based materials design

Earlier DFT calculations [1,2] have been able to identify three types of structural modification (as summarized in Fig. 3); each have their own special role to play in the materials-design strategy to meet the major challenges we have identified in the course of this work to improve the electrochemical performance of $\text{Li}_2\text{FeSiO}_4$:

- 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.

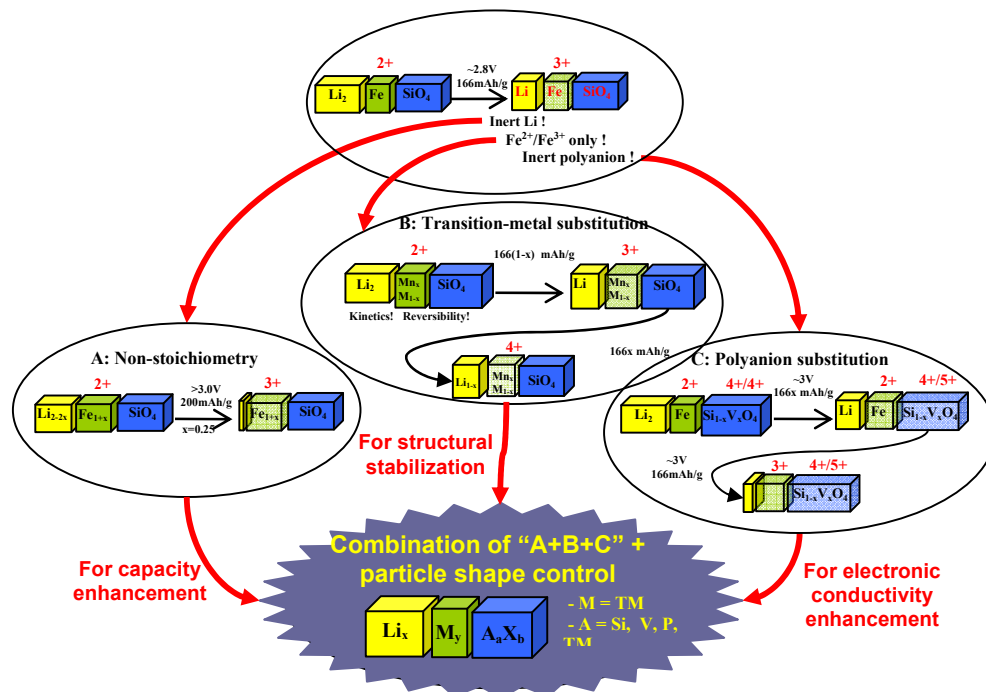


Figure 3: A schematic of the materials design strategy exploited in the project.

Charge transport in $\text{Li}_2\text{FeSiO}_4$

Earlier work has shown that mixing of the Li- and Fe-site occupations is an important structural feature in determining the electrochemical properties of $\text{Li}_2\text{FeSiO}_4$ [3]. Preferred Li^+ ion diffusion pathways and activation barriers for migration have thus been estimated from DFT calculations for both the un-mixed (SG Pmn2₁) and mixed (β - $\text{Li}_2\text{CoSiO}_4$ structure: SG Pbn2₁) models for $\text{Li}_2\text{FeSiO}_4$ [4]; see also the Year 2 report. This latter structure corresponds to the situation where 100% of the Fe and Li site-occupations are reversed; see Fig. 4. 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 LiFePO_4 - explaining the higher polarization on low-temperature cycling of $\text{Li}_2\text{FeSiO}_4$; see later. 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.

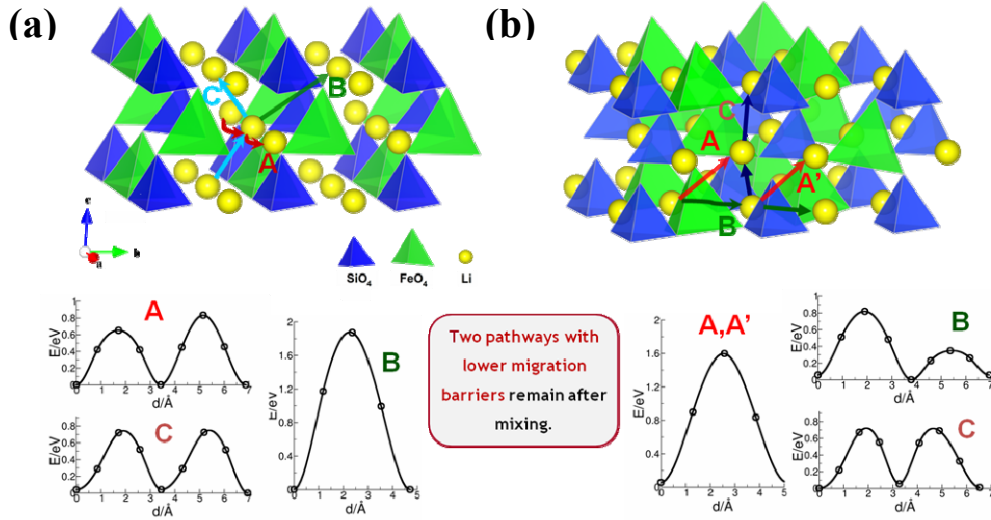


Figure 4: Li^+ migration pathways with corresponding energy profiles calculated for “un-mixed”(a) and “mixed”(b) Li/Fe-site models for the $\text{Li}_2\text{FeSiO}_4$ structure.

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. 5.

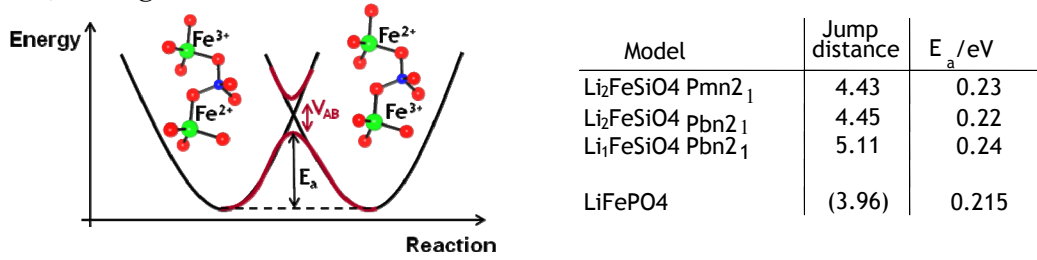


Figure 5: Electron transfer between Fe^{2+} and Fe^{3+} according to Marcus theory [5] is shown schematically for $\text{Li}_2\text{FeSiO}_4$ (left). The calculated activation energies E_a and polaron jump distances are shown in the Table (right), together with data reported for LiFePO_4 .

The electron hopping rate in $\text{Li}_2\text{FeSiO}_4$ is low, due mainly to the 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 $\sim 0.3\text{eV}$. A balance must clearly be found between the various possible substitution strategies.

Stabilization of the $\text{Li}_2\text{MnSiO}_4$ structure

The structure of $\text{Li}_2\text{MnSiO}_4$ (SG Pmn2₁) is now widely known to be unstable on deep delithiation [7-11]. Our calculations show that the Pmn2₁ structure of $\text{Li}_2\text{MnSiO}_4$ cannot be stabilized by the substitution of SiO_4^{4-} for other anion-types (with different ion-size and charge) like VO_4^{3-} and GeO_4^{4-} .

2. Recent advances in synthesis

A wide range of techniques have been used in the course of our work to synthesize silicate-based materials. Some features worthy of mention are:

(a) In a careful systematic study, the *solid-state synthesis* of $\text{Li}_2\text{FeSiO}_4$ was found to be highly sensitive to the nature of the reducing gas and amount of carbon-additive used [12,13].

(b) *Hydrothermal synthesis* of $\text{Li}_2\text{FeSiO}_4$ has also now produced material with good first-cycle capacity and stable cycling – even under sub-optimal conditions.

(c) A *solvothermally-assisted sol-gel process* has also been used with considerable success; see Fig. 6. 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 the 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 for $\text{Li}_2\text{FeSiO}_4$ could indeed result in elongated particles (Fig. 8).

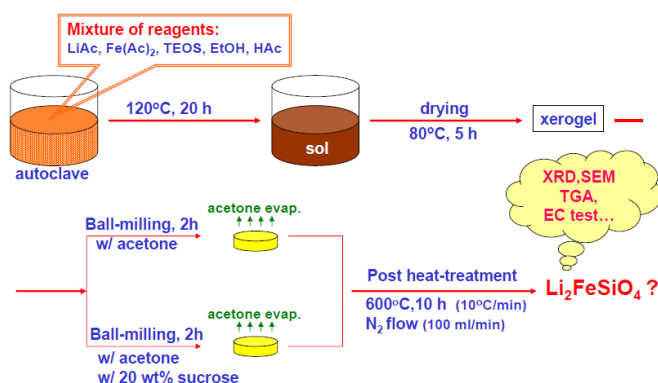


Figure 6: A schematic of the solvothermally-assisted sol-gel synthesis method used.

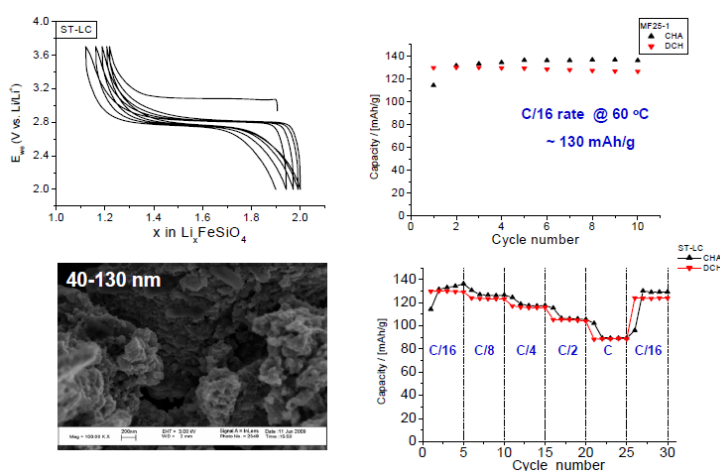


Figure 7: Cycling curves, capacities, morphology and rate performance (top-left to bottom-right) obtained for $\text{Li}_2\text{FeSiO}_4$ synthesized by the solvothermally-assisted sol-gel technique.

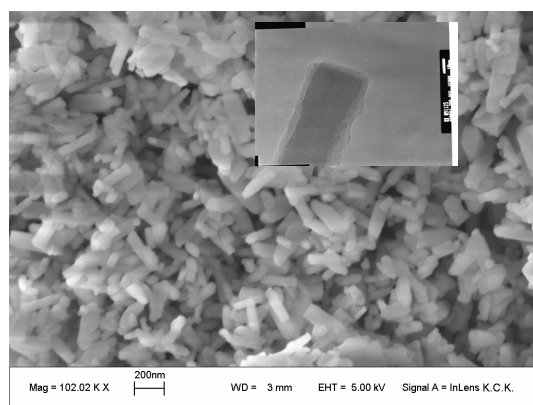


Figure 8: SEM image of the rod-shaped $\text{Li}_2\text{FeSiO}_4$ nanoparticles. The inset is a TEM image of a particle with a diameter of only 30nm.
 (d) Microwave-assisted synthesis [14,15] has also given encouraging results with greatly shortened synthesis times (Fig. 9); this is critical for a viable large-scale industrial process.

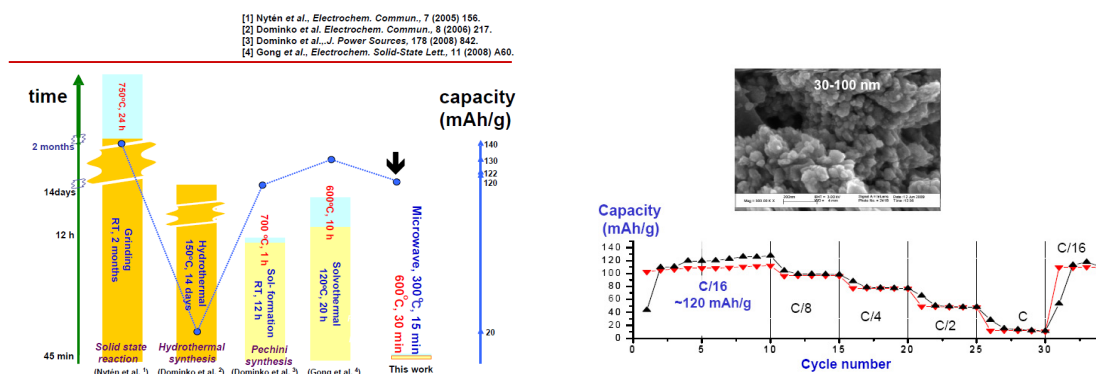


Figure 9: The dramatically shortened synthesis times realized by microwave-assisted synthesis (left), and the resulting rate performance of the resulting $\text{Li}_2\text{FeSiO}_4$ material (right) for process times in the minutes range, *cf.*, our first successful solid-state syntheses took two months with only marginally better results.

3. New cathode materials

Work is continuing within the areas reported on after *Year 2*; for example:

- *Mn*-substitution into $\text{Li}_2\text{FeSiO}_4$
- *Non-stoichiometric systems*: $\text{Li}_{2-2x}\text{M}_{1+x}\text{SiO}_4$, $M=\text{Fe}, \text{Mn}, \text{Co}$
- *Polyanion-substituted systems of type* $\text{Li}_2\text{Fe}(\text{SiO}_4)_{1-x}(\text{XO}_4)_x$ for $X=\text{V}, \text{Ge}$

These results will be summarized in their entirety in the *Final Report* in August 2010.

The new areas of investigation during *Year 3* have been:

(a) A *bystander-ion* system.

(b) Experimental work is continuing on *non-stoichiometric* lithium iron silicates (made by solvothermally-assisted synthesis; see above) for $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$, $x=0.25$ - theoretical capacity ~ 200 mAh/g. The material exhibits a much improved capacity compared to $\text{Li}_2\text{FeSiO}_4$; see *Year 2* report. However, some severely handicapping difficulties were encountered in establishing the *precise structure and phase composition* of this material. *We do not publish until we are sure!* Fresh ND powder data for the $x=0.25$ case have recently been collected to finally solve this problem. Data treatment is underway. Meanwhile, powerful support to the ND study is being given by *Mössbauer spectroscopy* applied to this same material. This can establish the structural situation of the various Fe-species present in the sample (*Table II*). In total, five different Fe-sites have been identified: **1** – the familiar Fe-site in $\text{Li}_2\text{FeSiO}_4$; **2** - an Fe-site near an Li-vacancy as expected in non-stoichiometric systems; **3** - Fe^{3+} in wüstite; **4&5** - Fe^{3+} species in $\text{Li}_2\text{FeSiO}_4$.

Table II: Isomer shifts (δ), quadrupole splittings (Δ) and relative concentrations (I %) from Mössbauer spectroscopy studies of the $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$, $x=0.25$ system.

Sites	1 & 2			3			4 & 5		
	δ	Δ	I	δ	Δ	I	δ	Δ	I
$\text{Li}_2\text{FeSiO}_4$	0.96	2.42	83	0.91	0.51	17			
$\text{Li}_{1.5}\text{Fe}_{1.25}\text{SiO}_4$ (solid- state route)	0.96	2.43	46	1.03	0.42	12	0.24	0.74	32
	1.16	2.80	10						
$\text{Li}_{1.5}\text{Fe}_{1.25}\text{SiO}_4$ (solvothermal route)	1.00	2.40	32	-	-	-	0.68	0.30	6
	1.17	2.84	18						

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 more complete understanding of this surface-film formation on $\text{Li}_2\text{FeSiO}_4$ cathodes has now been achieved for a wide range of different electrolyte/salt systems using highly painstaking X-Ray Photoelectron Spectroscopy (XPS); see *Fig. 10*.

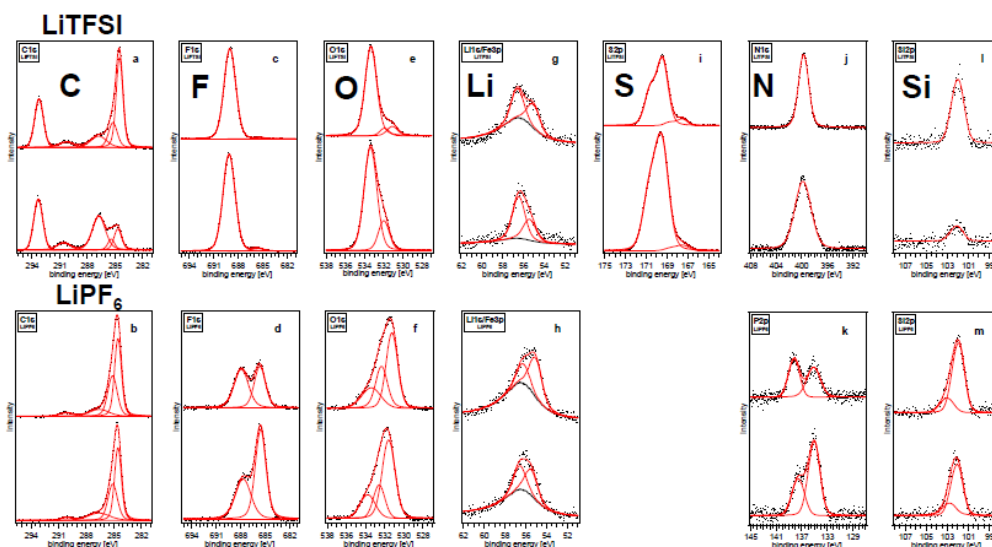


Figure 10: XPS spectra from a systematic study of lithiated (top spectrum in each rectangle) and delithiated (bottom) carbon-coated $\text{Li}_2\text{FeSiO}_4$ electrodes cycled with 1M LiTFSI EC:DEC (2:1) and 1M LiPF₆ EC:DEC (2:1) electrolytes.

A systematic study has also been 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 LiPF₆, LiBOB, LiTFSI, LiTDI and LiPDI; the latter two salts are new; see [16]. Some general conclusions can be drawn:

- **LiPF₆:** 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 is formed, giving excellent and consistent electrochemical performance; the dynamic changes observed are state-of-charge dependent.

To summarize: Yet again, we find convincing confirmation of the intrinsic high stability of the functioning $\text{Li}_2\text{FeSiO}_4$ cathode system – at least equal to that of LiFePO_4 . 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.

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

As brought up in last year’s report, we have felt it urgent to continue to address the critical issue of the *cyclability* of a $\text{Li}_2\text{FeSiO}_4$ positive electrode vs. a graphite negative electrode - in so-called “whole-cell” configuration. If $\text{Li}_2\text{FeSiO}_4$ is not able to function in conjunction with a graphite negative electrode, its future as a Li-ion battery cathode material is threatened; graphite is the material of choice in virtually all of today’s commercial Li-ion battery concepts. Such studies tend to come very late in the development of cathode materials; most research is done on cells

using Li-foil as negative electrode – so-called “half-cells”. Indeed, from an extensive survey of the cycling performance of such “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, we could conclude that, although Li₂FeSiO₄ cycles well in all half-cells using conventional electrolytes, *problems most certainly arise* in cycling against a graphite negative electrode. This is well illustrated in *Fig. 11*, which shows the cycling of a half- and whole-cell at 60°C; there is no reversible capacity available from the whole-cell.

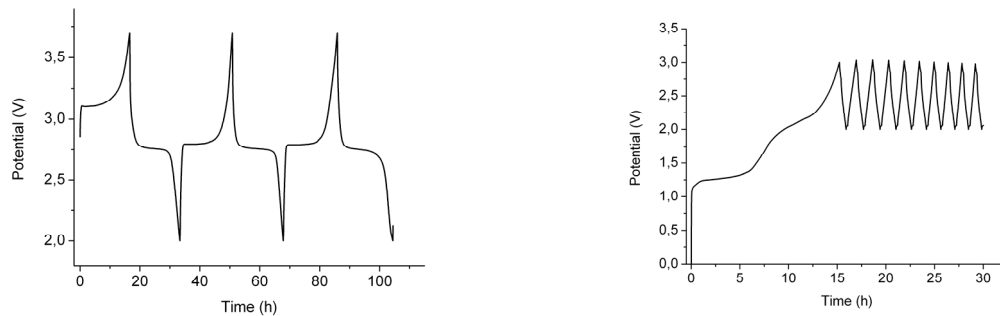


Figure 11: The potential profile of Li₂FeSiO₄ cycled at 60°C against metallic lithium (left) and graphite (right).

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.

Careful cell-balancing was ultimately able to give an operating whole-cell (*Fig. 12*) after:

- Optimizing the cycling temperature.
- Optimizing the electrolyte to be used at this temperature.

To our knowledge, this is the *first whole-cell demonstrator* exploiting a Li₂FeSiO₄ cathode. Though far from optimization, these demo-cells holds great promise for the future. A number 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 – likewise.

Li₂FeSiO₄-based Li-ion batteries retain their attraction; they are now being studied in most countries engaged in Li-ion battery research.

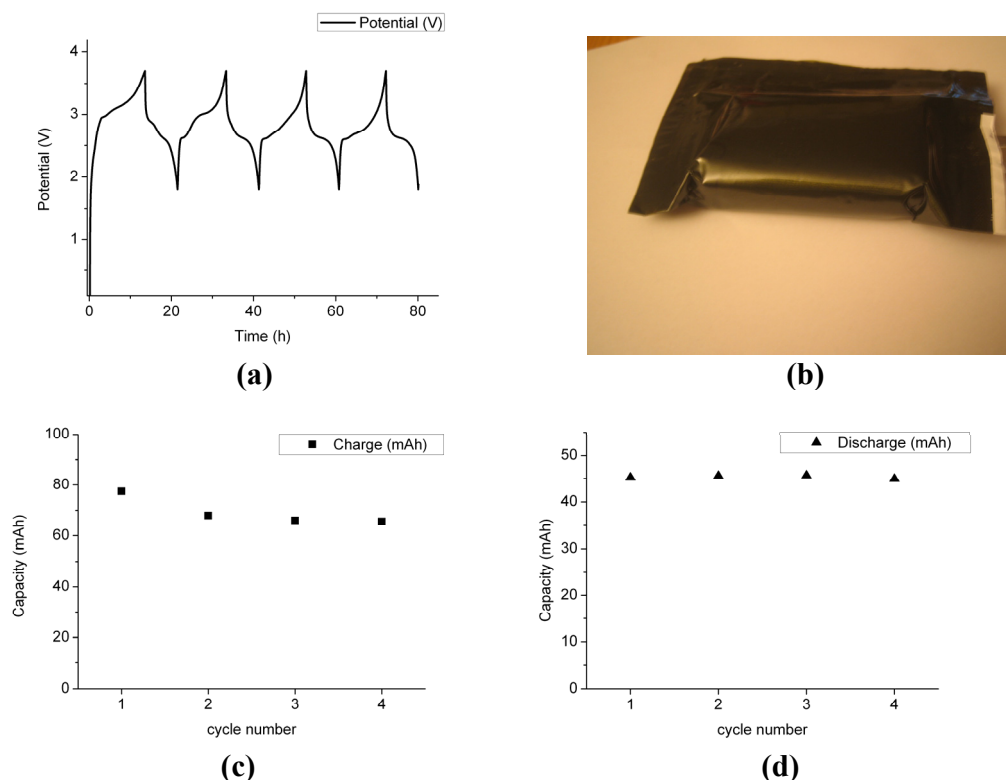


Figure 12: A “successful” voltage cycling profile (a) for a prismatic 80 mAh demonstration whole-cell (b) with an $\text{Li}_2\text{FeSiO}_4$ cathode and a graphite anode. Charge and discharge capacities (c and d) for only 4 test-cycles at constant current.

Future Plans

In the three months which remain of the project, we plan to do the following:

- Make a final assessment of the viability of the *non-stoichiometric* forms of $\text{Li}_2\text{FeSiO}_4$, and finally *solve their crystal structures*.
- Explore further the possibilities of *controlling particle-morphology* as a means to improve electrochemical performance.
- Time permitting – make a larger-scale *whole-cell demonstration* Li-ion battery using the most attractive silicate-based cathode material to emerge from the project.

Progress

The reduction in GHG emissions on a global scale from the transport sector has today become perhaps the most pressing environmental challenge 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 (sun, wind, water, ...) - is the obvious solution. The successful development of *large-scale Li-ion batteries* of the type envisioned in this project will have a long-lasting influence on the development of our planet. It is also often ignored that, at the broader level of energy supply, much larger Li-ion battery concepts than those needed for EVs could be used to store “green” electrical energy originating from renewable sources. This electrical energy reserve can then be used to charge our EVs, as well as heat and light our homes, *etc.*

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Publications 2009-2010:

1. Ensling, D., Stjerndahl, M., Nyten, A., Gustafsson, T. & 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 (2009) 82.
2. Larsson, P., Ahuja, R., Liivat, A. & Thomas, J. O. *Structural and electrochemical aspects of Mn substitution into $\text{Li}_2\text{FeSiO}_4$ from DFT calculations.* *Comp. Mater. Sci.*, 47 (2010) 678.
3. Liivat, A. and Thomas, J.O., *Li-ion migration in LFS cathode materials: a DFT study.* *Solid State Ionics* (2009), doi:10.1016/j.ssi.2009.12.009
4. Kam, K.C., Gustafsson, T. & Thomas, J.O., *Synthesis and electrochemical properties of nano-structured $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathode materials for Li-ion batteries.* *Solid State Ionics* (2010), doi:10.1016/j.ssi.2010.03.030
5. Liivat, A. & Thomas, J.O., *A DFT study of VO_4^{3-} polyanion substitution into the Li-ion battery cathode material $\text{Li}_2\text{FeSiO}_4$.* Submitted to: *Comp. Mater. Sci.*, (2010)
6. Lo M.F., EuroMaster Thesis: Sept. 2009, *Solvothermal, Microwave and Polyol Medium Synthesis of $\text{Li}_2\text{FeSiO}_4$.*

International conference presentations: 2009-2010

**At: International Conference on Solid State Ionics, Toronto, Canada,
28 June - 3 July 2009:**

- *An XPS study of surface-film formation on $\text{Li}_2\text{FeSiO}_4$ cathodes for different salt/solvent combinations.* Ensling, D., Jiang, Y., Gustafsson, T. and Thomas, J.O. (Invited oral)
- *Li-ion battery cathodes based on iron silicates,* Kam, K.C., Liivat, A. and Thomas, J.O. (Oral)
- *Li-ion transport mechanisms in orthosilicate-type cathode materials: a DFT study.* Liivat, A., Kam, K.C. and Thomas, J.O. (Oral)

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. (Oral)
- *VO_4^{3-} polyanion substitution into $\text{Li}_2\text{FeSiO}_4$: a DFT-study.* Kam, K.C., A. Liivat, A., and Thomas, J.O. (Poster)

At: Lithium Battery Discussion on Electrode Materials, Arcachon, France, 20-25 September 2009:

- *How do the silicates fit in?* J. O. Thomas. (Invited oral)
- *The Li-ion extraction/re-insertion mechanism in $\text{Li}_2\text{FeSiO}_4$.* Armstrong, A.R., Bruce, P.G., Gustafsson, T. and Thomas, J.O. (Poster)
- *Improving silicate-based cathode materials: insights from DFT modelling.* Liivat, A. and Thomas, J.O. (Poster)
- *Silicate-Based Cathode Materials: Synthesis and Characterization.* Kam, K.C., Liivat, A., Gustafsson, T. and Thomas, J.O. (Poster)
- *Combined SXPS and SXAS study of the electrochemical intercalation reaction of $\text{Li}_2\text{NiTiO}_4$ Cathodes.* Ensling, D., Kuezman, M., Dominko, R., Gustafsson, T., Thomas, J.O. and Gaberscek, M. (Poster)
- *Surface-film formation on $\text{Li}_2\text{FeSiO}_4$ 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, $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{SiO}_4$,* Kam, K.C., Liivat, A., Ensling, D., Gustafsson, T. and Thomas, J.O. (Oral)
- *A new cathode material for Li-ion batteries with the possibility of extracting two Li-ions per TM-atom.* Kuezman, M., Ensling, D., Dominko, R., Jamnik, J., Gustafsson, T., Thomas, J.O. and Gaberscek, M. (Oral)

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 oral)

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 oral)

Submitted (and accepted) contributions to 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.
- *Inexpensive synthesis of $\text{Li}_2\text{FeSiO}_4$ for up-scaled LIB cathodes.* Tan, S., Kam, K.C., Thomas, J.O. and Gustafsson, T.

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