A Quantum Leap Forward for Li-Ion Battery Cathodes

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Objective
The aim of this research is to develop a revolutionary new iron silicate-based active cathode material that can deliver energy and power densities in excess of those available from currently used materials in Li-ion batteries, and that is also significantly cheaper and more environmentally acceptable.

Background
In order for electric vehicles to have the range and convenience that current combustion engine vehicles provide, improvements in battery technology are necessary. Research into Li-ion batteries has focused on developing non-toxic, stable, and scalable cathode materials with high specific capacity. Silicates are attractive as cathode materials, because they are intrinsically stable and can accommodate a range of transition metal ions. For example, Li$_2$FeSiO$_4$ can substitute Fe (which realistically can only pass between Fe$^{2+}$ and Fe$^{3+}$) with another transition-metal ion that can undergo two-electron redox conversions and thereby facilitate the removal of (2Li$^+ + 2e^-$) from the material, producing an accompanying capacity increase. Preliminary work on a mixed Fe/Mn system, Li$_2$(Fe$_{1-x}$Mn$_x$)SiO$_4$, shows promise of such a redox reaction as shown in the equation:

$$\text{Li}^+_{2(\text{Fe}^{(II)}_{1-x}\text{Mn}^{(II)}_x)}\text{SiO}_4 \gg \text{Li}^+_{1-x}(\text{Fe}^{(III)}_{1-x}\text{Mn}^{(IV)}_x)\text{SiO}_4 + (1+x)\text{Li}^+ + (1+x)e^-$$

The schematic charge/discharge curve (see Figure 1) illustrates the gain to be made in following this strategy for the case of $x = 0.5$; the theoretical capacity of the resulting material would

![Schematic charge/discharge curve](image)

Figure 1: Preliminary work on a mixed Fe/Mn system for battery cathodes illustrates the potential for the material to have more than one redox reaction.
increase dramatically from 170 to 255 mAh/g. Unfortunately, initial material tests have shown hysteresis and some structural disruption, indicating that this performance is not sustainable. The challenge in developing these batteries is discovering structural/chemical conditions that can promote a reversible change in oxidation state (greater than one) in the transition-metal ions of the cathode material, and finding ways to modify the structural environment of the transition-metal ions to accommodate these changes.

**Approach**

Activities in this project will begin with screening a broad range of silicate-based materials and their synthesis techniques – guided by indications given by fundamental Density Function Theory (DFT) calculations. The best synthesis method(s) and material type(s) will be selected and fine-tuned to optimize both electrode and cell design in order to arrive at a final set of demonstration Li-ion battery prototypes. The project will study a family of materials not previously studied in the context of battery cathodes.

To address the materials challenges of this project, the following approaches will be used individually or in combination:

- **Introduction of nanoparticles** to increase the “tolerance” of the lattice to the repeated entry and subsequent exit of a large amount of intercalated lithium and the accompanying change in redox state.
- **Use of inert (“bystander”) cations** to pin down the structure at a level where they will not seriously reduce the ultimate capacity. Examples include Mg\(^{2+}\) and Ca\(^{2+}\), which can also be used to change the lattice size to optimize the geometry of the diffusion bottlenecks within the lattice. The presence of such “bystander” ions is likely to decrease the voltage, thereby offering a potential pathway to tuning the voltage obtained. Indications of the viability of such a strategy have been demonstrated from preliminary DFT calculations.
- **Screening and testing combinations of “inert” buffering ions or intervening organic species** that are also present.

Initial DFT calculations will indicate the potential effects from controlled doping of the basic Li\(_2\)FeSiO\(_4\) material to optimize electrochemical performance. Calculations will be performed to reproduce the effects of the modification approaches described above.

A wide range of conventional synthesis techniques (solid-state, solid-gel, carbothermal synthesis, hydrothermal synthesis, precipitation, etc.) will be used for the iterative preparation of phase-pure materials based on Li\(_2\)M\(_2\)SiO\(_4\) (where M is any selected combination of transition-metal and bystander ion), and for subsequent structural and electrochemical screening. The goal is to achieve phase-pure active particles with particle diameters of 20-30nm, both in an “uncoated” form and also when embedded in an electronically conducting (carbonaceous) matrix. The preparation of these composite networks is highly material-specific, so many routes will need to be tested to reach an optimal composite architecture.

Two main techniques (powder X-ray diffraction and electrochemical performance screening) will be used initially to screen the structure, phase-purity and electrochemical performance of the materials successfully synthesized. The most promising materials to emerge will be characterized in terms of their macro- and microscopic structures and their more detailed electrochemical performance under a range of conditions. Extensive experimental techniques will be used.

Fabrication and testing of Li-ion battery prototypes using the most promising materials will be made using an in-house battery fabrication pilot-line. The line has been developed for basic research purposes and operates under the prevailing conditions of commercial Li-ion battery production.