Silicate cathodes for lithium batteries: alternatives to phosphates?

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Polyoxanion compounds, particularly the olivine-phosphate LiFePO₄, are receiving considerable attention as alternative cathodes for rechargeable lithium batteries. More recently, an entirely new class of polyoxanion cathodes based on the orthosilicates, Li₂MSiO₄ (where M = Mn, Fe, Co), has been attracting growing interest. In the case of Li₂FeSiO₄, iron and silicon are among the most abundant and lowest cost elements, and hence offer the tantalising prospect of preparing cheap and safe cathodes from rust and sand! This Highlight presents an overview of recent developments and future challenges of silicate cathode materials focusing on their structural polymorphs, electrochemical behaviour and nanomaterials chemistry.

1. Introduction

For the next generation of rechargeable lithium batteries, there is intensive research activity targeted on developing new electrode materials, particularly for large-scale use in hybrid electric or pure electric vehicles and in stationary energy storage of solar/wind power [1-3]. Polyoxanion compounds are receiving considerable interest as alternative cathodes to the conventional intercalation oxides, layered LiCoO₂ or spinel LiMn₂O₄. The strong binding of the oxygen within polyoxanions enhances stability and thus safety, compared with transition metal oxides. The electronic inductive effect shifts the d-electrons of the transition metal ions and hence the redox potentials, providing a means of tuning the latter. Phosphate materials, particularly LiFePO₄, have been extensively studied and continue to be important [2,3].

More recently, a new class of polyoxanion cathodes based on the orthosilicates, Li₂MSiO₄ (where M = Mn²⁺, Fe³⁺, Co²⁺), has been attracting significant attention [4-34]. The relatively strong Si-O bonds promote similar lattice stabilization effects to the phosphate bonds found in LiFePO₄. Of these silicates, the most studied is Li₂FeSiO₄, with iron and silicon being among the most abundant and lowest cost elements. Indeed, developing cheap, sustainable and safe cathode materials is a prime target for large scale lithium batteries.

A key feature of the Li₂MSiO₄ system is that, in principle, extraction of two lithium ions is possible for a two electron redox process (i.e., operating on both M³⁺/M⁴⁺ and M⁵⁺/M⁶⁺ redox couples) especially for the Mn system; this should produce a higher capacity (e.g. above 300 mAh/g for Li₂MnSiO₄) than the olivine phosphates in which one lithium at most can be extracted.

Although numerous examples are cited, it is beyond the scope of this short review to give an exhaustive summary of all the studies in this highly active field. Rather, this article highlights recent developments of silicate-based cathodes with emphasis on their crystal structures, electrochemical behaviour and nanomaterials chemistry.

2. Polymorphism and Defects

Li₂MSiO₄ compounds (M = Fe, Mn, Co) belong to a large family of materials known as the tetrahedral structures [35,36]. These structures are composed of tetragonally packed oxide ions (a distorted form of hexagonal close packing) within which half the tetrahedral sites are occupied by cations, such that face sharing between the pairs of tetrahedral sites is avoided. The cations can order within the tetrahedral sites in different ways and various structural distortions are possible, leading to a rich and complex polymorphism, as summarised below.

The tetrahedral structures may be divided into two families, designated β and γ (related to the β- and γ polymorphs of Li₃PO₄). In the β structure all the tetrahedra point in the same direction, perpendicular to the close-packed planes, and share only corners with each other, shown in Figs 1(a), (b). In the case of the γ polymorphs, the tetrahedra are arranged in groups of three with the central tetrahedron pointing in the opposite direction to the outer two, with which it shares edges (Figs 1(c),(d),(e)). Where both β and γ polymorphs exist for a given compound the latter is stable at higher temperatures, with the β to γ transformation involving inversion of half the tetrahedral sites [36]. Several variants of both β and γ exist, involving either ordering or distortions of the parent structures; they are designated β₁, β₁I, γ₀, γ₁, γ₂ (Fig. 1). In many instances these phases may be quenched to room temperature, where they exhibit long-term stability.

Li₂FeSiO₄ Several structures have been proposed to describe Li₂FeSiO₄. The first was reported by Nyten et al [5] who suggested an orthorhombic structure (based on β-Li₃PO₄), with space group Pmmn (Fig. 1a). In this structure chains of Li₂O tetrahedra run along the a direction parallel to chains of alternating FeO₂ and SiO₂ tetrahedra. Later, Nishimura et al. [7] reported the structure of Li₂FeSiO₄ prepared at 800°C using a monoclinic space group P2₁. The structure has been designated by these authors as γ₁, Fig. 1(c). It differs from the other γ structures in that there are no edge sharing trimers of tetrahedra; instead one set of Li₂O tetrahedra are arranged in edge sharing pairs with FeO₂ tetrahedra, whilst the other set of Li₂O tetrahedra forms edge sharing pairs with itself, Fig. 1(c). More recently this description has been simplified using the higher symmetry space group P2₁/n [7b,17].

Sirisopanaporn et al [16] have described the crystal structure of a new γ₁Fe-polymorph of Li₂FeSiO₄, Fig 1(e), obtained by quenching from 900°C; the structure was established by electron microscopy, XRD, and neutron diffraction; it is
isostructural with Li$_2$CdSiO$_4$ (space group $Pmnb$), and differs from the $\gamma_s$ structure obtained by quenching from 800°C [7]. A simple $\beta_{II}$ polymorph (Fig. 1(a)), space group $Pmn2_1$, may be prepared by hydrothermal synthesis at low temperature [8].

![Diagram](image1)

It has been demonstrated that variations in the FeO$_4$ geometry (orientation, size, and distortion) influence the equilibrium potential measured during the first oxidation of Fe$^{2+}$ to Fe$^{3+}$ in all polymorphs. Shorter and hence stronger (more covalent) Fe-O bonds result in greater splitting in energy between bonding and anti-bonding states, lowering the Fe$^{2+}$/Fe$^{3+}$ redox potential vs. Li$^+$/Li$^0$ (Fig. 2) [18]. Magnetic susceptibility measurements [6] indicate that Li$_2$FeSiO$_4$ powders prepared at 800 °C possess an antiferromagnetic ordering below $T_N = 25$ K due to long range Fe-O-Li-O-Fe interactions.
incorporation on the Si site with Li interstitial compensation; this suggests a possible synthesis-doping strategy of introducing additional lithium into Li$_2$MnSiO$_4$ for higher capacities. Recent DFT-based studies have investigated the electronic structure, structural stability and ion substitution in the Li$_2$MSiO$_4$ materials [31].

**3. Electrochemistry and nanomaterials**

**Li$_2$FeSiO$_4$.** The third member of the orthosilicate family of cathode materials, Li$_2$CoSiO$_4$, has received comparatively less attention [32-34]. Three polymorphic forms ($\beta_{II}$, $\beta_{III}$, and $\gamma_0$) have been prepared and investigated with powder diffraction and $^7$Li MAS NMR [32,33]. The $\beta_{II}$ (Pmn2$_1$) polymorph was obtained by hydrothermal synthesis (150 °C), and subsequent heat treatments yielded the $\beta_{III}$ (Pbnm2$_1$) form (700°C) and the $\gamma_0$ (P2$_1$/n) form (1100 °C then quenching from 850°C).

Rietveld refinement of X-ray and neutron powder diffraction patterns reveal antiseite disorder for $\beta_{II}$ with Li on the Co site and Co sharing the Li site (essentially an inverse $\beta_{II}$ structure analogous to inverse spinels), very moderate Li/Co mixing for $\beta_{III}$, and no mixing for $\gamma_0$. $^7$Li MAS NMR spectra have been recorded for the three forms, and the nature and number of signals were analyzed in relation to the site occupancies for each compound [33].

Most of the reported electrochemical studies were conducted at elevated temperatures (e.g. 60 °C) to improve the rate performance and increase capacity. Typical capacities are 120-140 mA h g$^{-1}$ in the voltage range below 4V vs. Li [Fig 4] [24, 28]. The cycling stability of the Li$_2$FeSiO$_4$ cathode after conversion to the $\beta$ phase is good [14]. However, due to low intrinsic conductivity, the rate performance needs to be improved to a similar degree to LiFePO$_4$ in order to become competitive for commercial applications. By analogy with LiFePO$_4$, the strategy has been to reduce the particle size and to use carbon coatings (Fig. 5) [4,8,14,22]. In practice, this strategy usually involves the addition of a carbon precursor (citrate anion, ethylene glycol, etc.) that also acts as a complexing agent promoting the formation of a homogeneous gel. The presence of carbon during heat treatment suppresses active particle growth and particle agglomeration [8,10].

Yang and co-workers have made a number of advances in synthetic methods; for example Gong et al [22] reported a carbon-coated Li$_2$FeSiO$_4$ material with uniform nanoparticles (~40-80nm) from a hydrothermal-assisted sol-gel process; this showed a discharge capacity of 160 mA h g$^{-1}$ at C/16 rate, and almost no capacity loss up to 50 cycles. Zhang et al [24] reported...
a sol-gel method based on citric acid to prepare Li$_2$FeSiO$_4$ in which the citric acid acts as both a chelating agent and a carbon source in the synthetic process; they observed a maximum discharge capacity of 153.6 mAh g$^{-1}$ in the third cycle, with 98.3% of this capacity retained after 80 charge-discharge cycles.

Manthiram and co-workers [28] have synthesized nanostructured Li$_2$FeSiO$_4$ and Li$_2$MnSiO$_4$ by a facile microwave-solvothermal process; they report that the Li$_2$FeSiO$_4$ nanocomposite exhibits good rate capability and stable cycle life, with discharge capacities of 148 mAh g$^{-1}$ at room temperature and 204 mAh g$^{-1}$ at 55°C, whereas Li$_2$MnSiO$_4$/C suffers from poor rate capability and drastic capacity fade. Capacities greater than 200 mAh g$^{-1}$ have been observed by several groups. Such capacities exceed the theoretical value for Fe$^{2+/3+}$ redox couple (166 mAh g$^{-1}$); the results have been interpreted as implying either Fe$^{4+}$ formation and/or electrolyte degradation.

Photoelectron spectroscopy (PES) has been used by Thomas and co-workers [5c] to examine the Li$_2$FeSiO$_4$ cathode surface extracted from lithium-ion batteries; a thin surface film is formed on electrochemical cycling of Li$_2$FeSiO$_4$ electrodes at 60°C using a LiIn(SO$_4$CF$_3$)$_2$ salt based electrolyte, with high salt stability and only small amounts of solvent reaction products. It is suggested that the excellent capacity retention observed (<3% over 120 cycles) during the first cycle is probably a result of this thin surface film [5c].

Li$_2$MnSiO$_4$. Li$_2$MnSiO$_4$ could be viewed as an attractive cathode material, in terms of energy density and possibility of >1-electron redox process since the higher manganese oxidation state Mn$^{4+}$ is more accessible than Fe$^{4+}$. Li$_2$MnSiO$_4$ is found to have a redox potential near 4.1V vs Li, but initial studies show substantial irreversible capacity loss [8-11]. In-situ XRD studies indicate that for Li$_2$FeSiO$_4$ cycling proceeds through a plateau relating to a two-phase mechanism, whereas lithium exchange from Li$_2$MnSiO$_4$ involves the formation of an amorphous phase along the oxidation plateau at approximately 4.1V (Fig. 6) [10,23].

Li et al [23] have reported the synthesis of a high capacity Li$_2$MnSiO$_4$/C nanocomposite material with good rate performance and a reversible capacity of 209 mAh g$^{-1}$ in the first cycle; their XRD and IR results also indicate that the poor cycling behavior might be due to an amorphization of the silicate.

**Fig. 4.** Electrochemical properties of Li$_2$FeSiO$_4$: (a) Discharge-charge curves for samples at C/20 rate. (b) Cycling performance at different current densities (marked as C-rates). [10, 14]

**Fig. 5.** SEM micrographs of Li$_2$FeSiO$_4$ obtained by a) modified Pechini synthesis method [10] and b) hydrothermal synthesis method [14].

**Fig. 6.** In-situ X-ray diffraction patterns and voltage profiles for Li$_2$MnSiO$_4$/C at C/50 rate [10] (a) Li$_2$MnSiO$_4$ (b) Li$_2$FeSiO$_4$. Bragg reflections marked with asterisk denotes in situ cell reflections.
material. Aravindan et al [30] have recently employed an adipic acid assisted sol–gel route to prepare \( \text{Li}_2\text{MnSiO}_4 \) nanoparticles, with their \( \text{Li}/\text{Li}_2\text{MnSiO}_4 \) cell delivering a stable discharge capacity profile (\( \sim 125 \text{ mAh g}^{-1} \)) for up to 50 cycles.

Due to problems with the pure Mn-based material, there have been recent studies on mixed-cation \( \text{Li}_2(\text{Fe,Mn})\text{SiO}_4 \) solid solutions [13,21]. Preliminary studies on mixed-metal materials suggest the use of the \( \text{Li}_2\text{Fe}_{0.8}\text{Mn}_{0.2}\text{SiO}_4 \) composition. The basic concept was to stabilize the local environment of Mn in tetrahedral coordination by introducing Fe as a “stabilizer”, in line with DFT-based calculations [9]. Gong et al [21] reported an optimal composition of \( \text{Li}_4\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4 \) that delivers high capacity (214 mAh g\(^{-1}\)) within a wide voltage window, but with serious capacity fade during cycling.

Studies on \( \text{Li}_2\text{Fe}_{0.8}\text{Mn}_{0.2}\text{SiO}_4 \) show good reversibility with a large voltage polarisation in the formation cycles [13]. Using in-situ Mössbauer spectroscopy and XANES it was shown that most of the iron was reversibly oxidised to Fe\(^{III}\), while only a part of the manganese was reversibly oxidised to Mn\(^{IV}\). Importantly, neither iron nor manganese in the tetravalent state was detected [13]. Future studies are likely to explore whether the performance of other mixed-metal solid solutions proves superior to the pure compounds as found in the case of the layered LiMO\(_2\) cathodes (e.g. \( \text{Li}(\text{Co}_{0.8}\text{Mn}_{0.2})\text{O}_2 \)) [2].

\( \text{Li}_2\text{CoSiO}_4 \). Lyness et al [32] show that the three polymorphs of \( \text{Li}_2\text{CoSiO}_4 \) exhibit electrochemical activity when ball-milled, although with severe capacity fading after a few cycles, which is also the case for the corresponding cobalt-based phosphate, \( \text{LiCoPO}_4 \). For the \( \beta \) polymorph, coating the as-prepared material with carbon switches on electrochemistry without the need for ball-milling and gives superior charge capacity (170 mAh h \(^{-1}\) = 1.1 Li per formula unit) and cyclability, compared with the same phase when ball-milled with carbon (Fig. 7). Only one Li could be extracted up to 4.6 V in agreement with theoretical predictions.

Gong et al [34] have prepared \( \text{Li}_2\text{CoSiO}_4 \) by a solution-hydrothermal route, and find reversible lithium extraction/insertion at 4.1 V vs Li, but limited to 0.46 lithium per formula unit for the \( \text{Li}_2\text{CoSiO}_4/C \) composite materials, with a reported charge capacity of 234 mAh g\(^{-1}\).

Fig. 7. Electrochemical properties of \( \text{Li}_2\text{CoSiO}_4 \): a) Variation of voltage with state of charge (Li content) on cycling the \( \beta \) polymorph carbon coated by the xerogel process at a rate of 10 mAg\(^{-1}\). Inset shows performance of uncoated material. b) Variation of discharge capacity with cycle number for the carbon-coated \( \beta \) polymorph cycled between 2.0 and 4.6 V at 10 mAg\(^{-1}\) [32].

4. Conclusions and future outlook

This review has highlighted an important class of polyoxyanion compounds based on the orthosilicates, \( \text{Li}_2\text{MSiO}_4 \) (where M = Mn, Fe, Co), which are attracting growing interest as possible low-cost and safe cathodes for new generations of rechargeable lithium batteries. It serves to illustrate the value of fundamental studies of new materials, including the synthesis and characterisation of silicate polymorphs. However, there are a number of important challenges facing the silicates before they could be considered as viable cathodes and especially as alternatives to \( \text{LiFePO}_4 \). The challenges have been discussed above and are summarised here.

(i) For all \( \text{Li}_2\text{MSiO}_4 \) compounds there are significant differences between the first charge and subsequent cycling, which is indicative of structural changes, possibly involving Li/M cation exchange. Further fundamental studies to investigate these structural changes are warranted. In addition to crystallographic studies of the average structure, increasing use of local structure techniques and computer modelling to probe local defects, nanoscale structures, and Li-ion conduction pathways, will be important. Efforts will doubtless be directed to the preparation of polymorphs that are stable from the outset to ensure the electrochemistry does not change on cycling.

(ii) Although the components, Fe, Mn, Si, are low cost, so also must the synthesis methods and their precursors, if truly low cost electrodes are to be obtained. Furthermore the synthesis methods must be scalable.

(iii) The rate capability needs to be improved. This will necessitate a better understanding of the origins of the low rate; especially studies of ionic and electronic transport and the kinetics of phase transitions. Optimising the rate performance will doubtless involve the synthesis of nanostructured materials, the control of particle size and morphology, and the use of chemical doping and surface coatings.

(iv) Higher capacities than are associated with one Li per formula unit (170 mAh g\(^{-1}\)) are desirable, preferably with higher voltages
such as those associated with Li$_2$MnSiO$_4$. Modifying the stoichiometric materials to enhance the Li composition range will be important.

(v) Most studies have concentrated on pure Li$_2$MgSiO$_4$ compositions, which are a necessary prelude to studying solid solutions of Li$_2$MgSiO$_4$ with mixed M of Fe, Mn and Co. It will be interesting to see whether the performance of such mixed-metal solid solutions proves superior to the pure phases as observed in the case of the layered LiMO$_2$ cathodes (e.g. Li(Co$_{1/3}$Mn$_{1/3}$Ni$_{1/3}$)O$_2$), and therefore of technological significance.

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