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HIGHLIGHT

Silicate cathodes for lithium batteries: alternatives to phosphates?

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Polyoxyanion compounds, particularly the olivine-phosphate $LiFePO_4$, are receiving considerable attention as alternative cathodes for rechargeable lithium batteries. More recently, an entirely new class of polyoxyanion cathodes based on the orthosilicates, Li_2MSiO_4 (where M = Mn, Fe, and Co), has been attracting growing interest. In the case of Li_2FeSiO_4, 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] Polyoxyanion compounds are receiving considerable interest as alternative cathodes to the conventional intercalation oxides, layered $LiCoO_2$ or spinel $LiMn_2O_4$. The strong binding of the oxygen within polyoxyanions enhances the stability and thus safety, compared with transition metal oxides. The electronic inductive effect shifts the d-states of the transition metal ions and hence the redox potentials, providing a means of tuning the latter. Phosphate materials, particularly $LiFePO_4$, have been

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extensively studied and continue to be important.[2,3]

More recently, a new class of polyoxyanion cathodes based on the orthosilicates, Li_2MSiO_4 (where $M = Mn^{2+}$, Fe^{2+}, and Co^{2+}), has been attracting significant attention.[4–34] The relatively strong Si–O bonds promote similar lattice stabilization effects to the phosphate bonds found in $LiFePO_4$. Of these silicates, the most studied is Li_2FeSiO_4, 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.

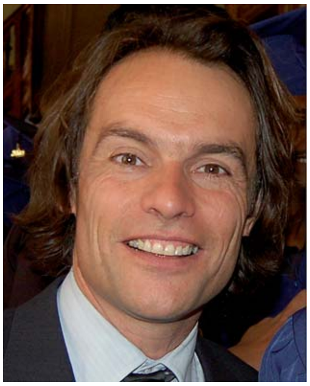
A key feature of the Li_2MSiO_4 system is that, in principle, extraction of two lithium ions is possible for a two electron redox process (*i.e.*, operating on both M^{2+}/M^{3+} and M^{3+}/M^{4+} redox couples) especially for the Mn system; this should produce a higher capacity (*e.g.* above 300 mA h g^{-1} for Li_2MnSiO_4) 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

Li_2MSiO_4 compounds (M = Fe, Mn, and 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 the 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 Li_3PO_4). 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 Fig. 1(a) and (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 (Fig. 1(c–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



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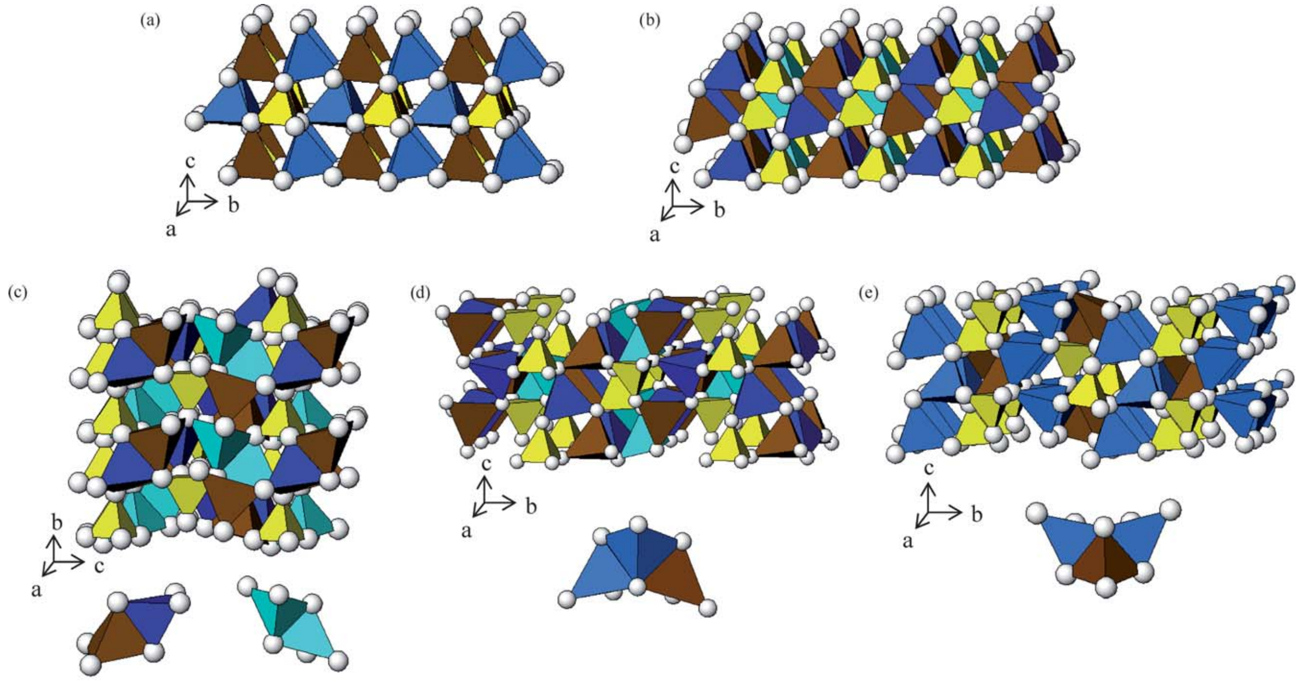

Fig. 1 Structures of Li_2MSiO_4 polymorphs; (a) β_{II} structure in which all the tetrahedra point in the same direction, perpendicular to the close-packed planes, and share only corners with each other; chains of LiO_4 along the *a*-axis and parallel to chains of alternating MO_4 and SiO_4, (b) β_I structure, all tetrahedra point in the same direction with chains of alternating LiO_4 and MO_4 tetrahedra along *a*, parallel to chains of alternating LiO_4 and SiO_4 tetrahedra, (c) γ_s structure, half tetrahedra pointing in opposite directions and contain pairs of LiO_4/MO_4 and LiO_4/LiO_4 edge-sharing tetrahedra (inset), (d) γ_0 structure in which 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; the group of 3 edge-sharing tetrahedra consist of the sequence Li–Li–M (inset), (e) γ_{II} structure in which the group of 3 edge-sharing tetrahedra consist of the sequence Li–M–Li (inset). SiO_4 (yellow); MO_4 (brown); LiO_4 (blue); light and dark blue tetrahedra represent crystallographically distinct Li sites.

structures; they are designated β_I, β_{II}, γ_0, γ_{II}, and γ_s (Fig. 1). In many instances these phases may be quenched to room temperature, where they exhibit long-term stability.

Li_2FeSiO_4

Several structures have been proposed to describe Li_2FeSiO_4. The first was reported by Nyten *et al.*[5] who suggested an orthorhombic structure (based on β-Li_3PO_4), with space group *Pmn*2$_1$ (Fig. 1(a)). In this structure chains of LiO_4 tetrahedra run along the *a* direction parallel to chains of alternating FeO_4 and SiO_4 tetrahedra. Later, Nishimura *et al.*[7] reported the structure of Li_2FeSiO_4 prepared at 800 °C using a monoclinic space group *P*2$_1$. The structure has been designated by these authors as γ_s, Fig. 1(c). It differs from the other γ structures in that there are no edge sharing trimers of tetrahedra; instead one set of LiO_4 tetrahedra are arranged in edge sharing pairs with FeO_4 tetrahedra, whilst the other set of LiO_4 tetrahedra forms edge sharing pairs with itself, Fig. 1(c). More recently this description has been simplified using the higher symmetry space group *P*2$_1$/*n*.[7b,17]

Sirisopanaporn *et al.*[16] have described the crystal structure of a new γ_{II}-polymorph of Li_2FeSiO_4, 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_2CdSiO_4 (space group *Pmnb*), and differs from the γ_s structure obtained by quenching from 800 °C.[7] A simple β_{II} polymorph (Fig. 1(a)), space group *Pmn*2$_1$, may be prepared by hydrothermal synthesis at low temperature.[8]

It has been demonstrated that variations in the FeO_4 geometry (orientation,

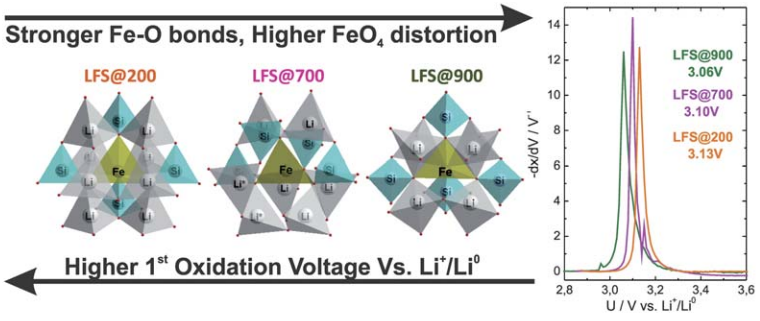

Fig. 2 Local environments around FeO_4 tetrahedra (in green) in the three polymorphs of Li_2FeSiO_4: β_{II} (LFS@200); γ_s (LFS@700); γ_{II} (LFS@900). (LiO_4 in grey, SiO_4 in blue) and derivative plots obtained from PITT in the first oxidation of these three polymorphs.[18]

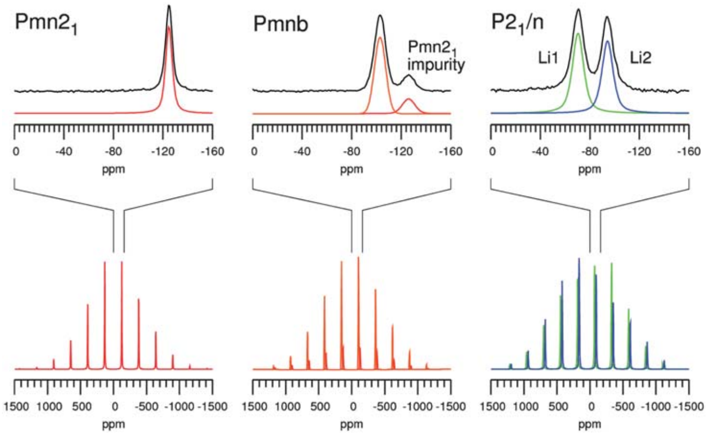

Fig. 3 ^{6}Li MAS NMR spectra of three Li_2MnSiO_4 polymorphs (after ref. 15). The upper part shows isotropic bands and lower part presents the entire manifolds of spinning sidebands.

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 the 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_2FeSiO_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.

Li_2MnSiO_4

From powder X-ray diffraction (XRD), Dominko *et al.*[8] proposed an orthorhombic β_{II} structure for Li_2MnSiO_4 (based on β-Li_3PO_4, space group *Pmn*2$_1$); they also pointed out the possibility of another γ_{II}-polymorph (*Pmnb*) detected by electron diffraction. XRD studies by Politaev *et al.*[19] reported a γ_0 structure with monoclinic symmetry (space group *P*2$_1$/*n*) based on γ-Li_3PO_4, similar to that reported for monoclinic Li_2CoSiO_4[32] (Fig. 1(d)); they also observed a small amount of Li/Mn cation exchange in Li_2MnSiO_4. Atomistic defect modelling studies on Li_2MnSiO_4[20] indicate that the most energetically favourable intrinsic disorder is the Li–Mn anti-site or cation exchange defect, suggesting a small population of Li on Mn sites and Mn on Li sites, dependent on synthesis routes and thermal history.

^{6}Li MAS NMR spectroscopy has proved to be a very useful tool to distinguish between different Li_2MnSiO_4 polymorphs.[15] Lithium nuclei occupying crystallographically inequivalent lithium sites within a single polymorph exhibited NMR signals at different and well resolved positions (Fig. 3).

Density functional theory (DFT) calculations[9] on orthorhombic Li_2MnSiO_4 predict that this phase is unstable on extraction of large amounts of lithium. Arroyo-de Dompablo *et al.*[12] also reported DFT calculations on the thermodynamic stability of Li_2MnSiO_4 polymorphs predicting that the lowest energy is found for the β-Li_3PO_4 based derivatives. Atomistic defect modelling studies[20] predict favourable Al^{3+} dopant incorporation on the Si site with Li interstitial compensation; this suggests a possible synthesis-doping strategy of introducing additional lithium into Li_2MnSiO_4 for higher capacities. Recent DFT-based studies have investigated the electronic structure, structural stability and ion substitution in the Li_2MSiO_4 materials.[31]

Li_2CoSiO_4

The third member of the orthosilicate family of cathode materials, Li_2CoSiO_4, has received comparatively less attention.[32–34] Three polymorphic forms (β_{II}, β_I, and γ_0) have been prepared and investigated with powder diffraction and

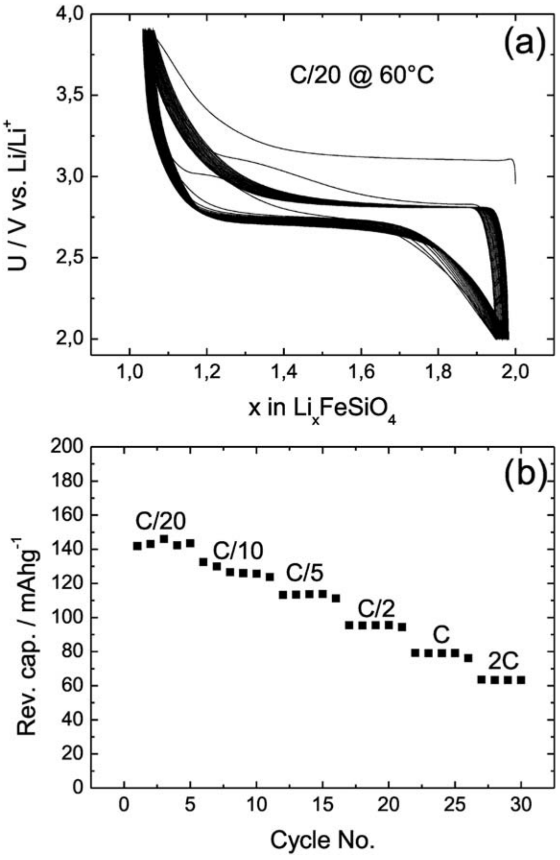

Fig. 4 Electrochemical properties of Li_2FeSiO_4; (a) discharge–charge curves for samples at C/20 rate. (b) Cycling performance at different current densities (marked as C-rates).[10,14]

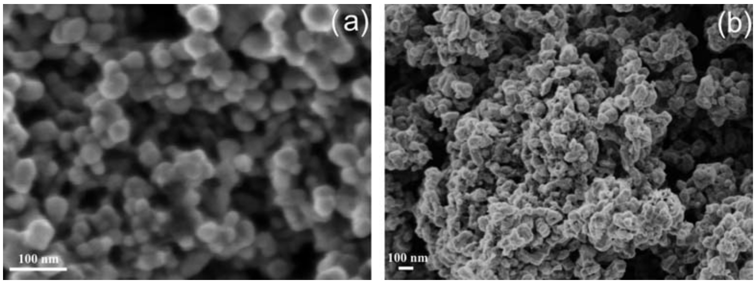

Fig. 5 SEM micrographs of Li_2FeSiO_4 obtained by (a) modified Pechini synthesis method[10] and (b) hydrothermal synthesis method.[14]

^{7}Li MAS NMR.[32,33] The β_{II} ($Pmn2_1$) polymorph was obtained by hydrothermal synthesis (150 °C), and subsequent heat treatments yielded the β_I ($Pbn2_1$) form (700 °C) and the γ_0 ($P2/n$) form (1100 °C then quenching from 850 °C). Rietveld refinement of X-ray and neutron powder diffraction patterns reveal antisite disorder for β_{II} with Li on the Co site and Co sharing the Li site (essentially an inverse β_{II} structure analogous to inverse spinels), very moderate Li/Co mixing for β_I, and no mixing for γ_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]

3. Electrochemistry and nanomaterials

Li_2FeSiO_4

Li_2FeSiO_4 was shown to undergo an initial charge at voltages above 3 V *vs.* Li while subsequent charges were at 2.84 V *vs.* Li.[5] Such a shift in potential suggested a change of structure, which was confirmed by X-ray diffraction and Mossbauer spectroscopy during the initial cycles. Studies on the cycled material by neutron diffraction identified conversion from the γ_s structure to a structure corresponding to the inverse β_{II} (originally observed for Li_2CoSiO_4, described above).[5a,18] Further studies to investigate such structural changes are warranted, and efforts will doubtless be directed towards the synthesis of polymorphs that are stable from the outset to ensure the electrochemistry does not change on cycling.

Most of the reported electrochemical studies were conducted at elevated temperatures (*e.g.* 60 °C) to improve the rate performance and increase the capacity. Typical capacities are 120–140 mA h g^{-1} in the voltage range below 4 V *vs.* Li (Fig. 4).[24,28] The cycling stability of the Li_2FeSiO_4 cathode after conversion to the β 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_2FeSiO_4 material with uniform nanoparticles (~40 to 80 nm) 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

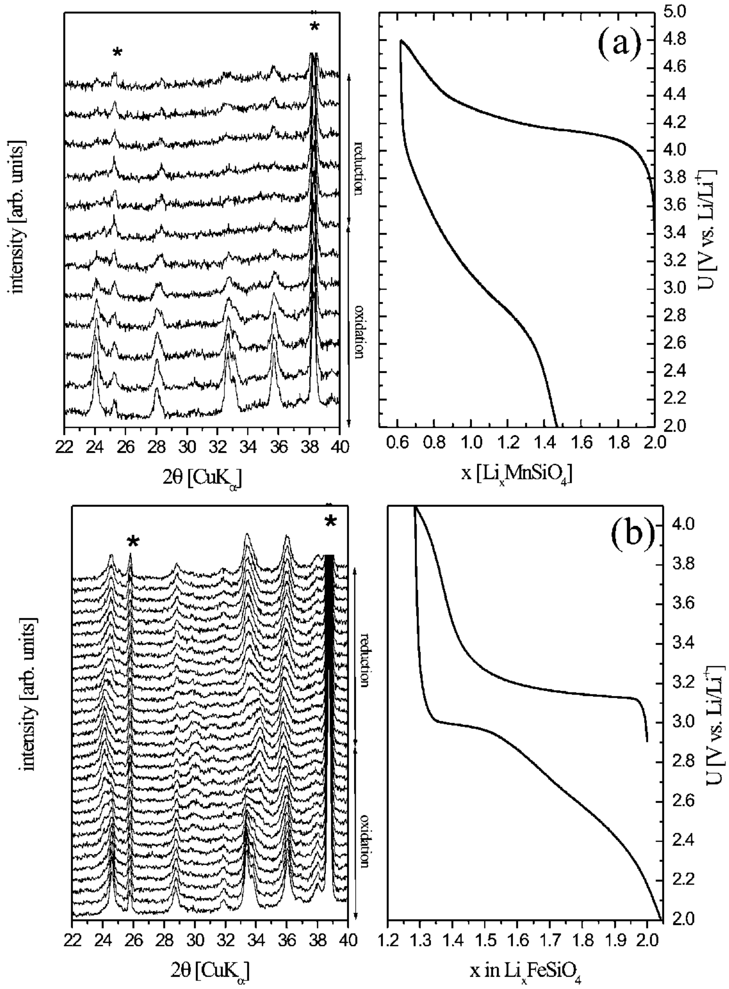

Fig. 6 *In situ* X-ray diffraction patterns and voltage profiles for Li_2MSiO_4/C at C/50 rate[10] (a) Li_2MnSiO_4 and (b) Li_2FeSiO_4. Bragg reflections marked with asterisk denotes *in situ* cell reflections.

based on citric acid to prepare Li_2FeSiO_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 mA h 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_2FeSiO_4 and Li_2MnSiO_4 by a facile microwave-solvothermal process; they report that the Li_2FeSiO_4/C nanocomposite exhibits good rate capability and stable cycle life, with discharge capacities of 148 mA h g^{-1} at room temperature and 204 mA h g^{-1} at 55 °C, whereas Li_2MnSiO_4/C suffers from poor rate capability and drastic capacity fade. Capacities greater than 200 mA h g^{-1} have been observed by several groups. Such capacities exceed the theoretical value for $Fe^{2+/3+}$ redox couple (166 mA h g^{-1}); the results have been interpreted as implying either Fe^{4+} formation[28] and/or electrolyte degradation[13].

Photoelectron spectroscopy (PES) has been used by Thomas and co-workers[5c] to examine the Li_2FeSiO_4 cathode surface extracted from lithium-ion batteries; a thin surface film is formed on electrochemical cycling of Li_2FeSiO_4 electrodes at 60 °C using a $LiN(SO_2CF_3)_2$ salt based electrolyte, with high salt stability and only small amounts of solvent reaction products. It is suggested that the excellent capacity retention observed (>97% over 120 cycles) during the first cycle is probably a result of this thin surface film.[5c]

Li_2MnSiO_4

Li_2MnSiO_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_2MnSiO_4 is found to have a redox potential near 4.1 V *vs.* Li, but initial studies show substantial irreversible capacity loss.[8–11] *In situ* XRD studies indicate that for Li_2FeSiO_4 cycling proceeds through a plateau relating to a two-phase mechanism, whereas lithium exchange from Li_2MnSiO_4 involves the formation of an amorphous phase along the oxidation plateau at approximately 4.1 V (Fig. 6).[10,23]

Li *et al.*[23] have reported the synthesis of a high capacity Li_2MnSiO_4/C nanocomposite material with good rate performance and a reversible capacity of 209 mA h 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 material. Aravindan *et al.*[30] have recently employed an adipic acid assisted sol–gel route to prepare Li_2MnSiO_4 nanoparticles, with their Li/Li_2MnSiO_4 cell delivering a stable discharge capacity profile (125 mA h g^{-1}) for up to 50 cycles.

Due to problems with the pure Mn-based material, there have been recent studies on mixed-cation $Li_2(Fe,Mn)SiO_4$ solid solutions.[13,21] Preliminary studies on mixed-metal materials suggest the use of the $Li_2Fe_{0.5}Mn_{0.5}SiO_4$ composition. The basic concept was to stabilize the local environment of Mn^{3+} 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 $Li_2Fe_{0.5}Mn_{0.5}SiO_4$ that delivers high capacity (214 mA h g^{-1}) within a wide voltage window, but with serious capacity fade during cycling.

Studies on $Li_2Fe_{0.8}Mn_{0.2}SiO_4$ 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^{III}. 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.* $Li(Co_{1/3}Mn_{1/3}Ni_{1/3})O_2$).[2]

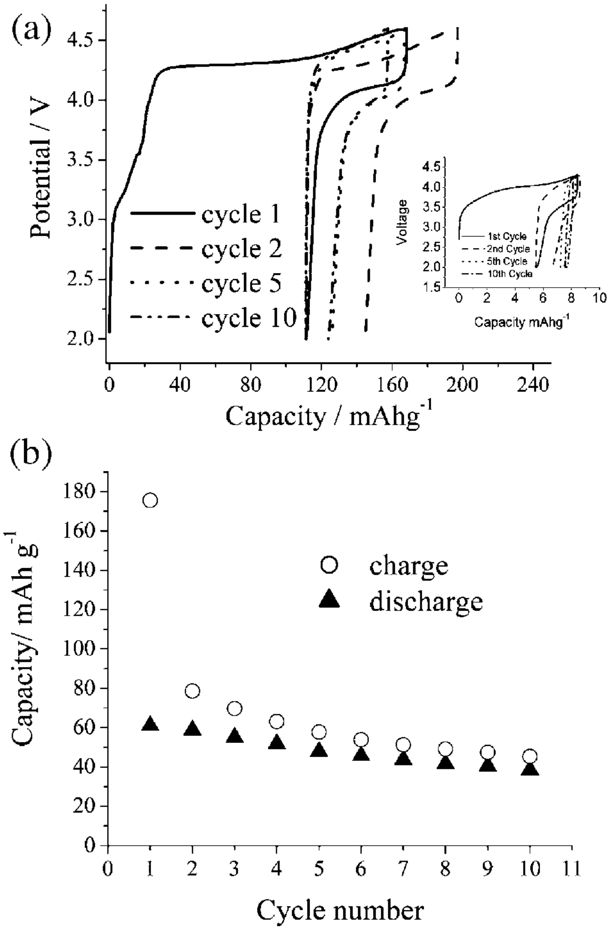

Fig. 7 Electrochemical properties of Li_2CoSiO_4; (a) variation of voltage with the state of charge (Li content) on cycling the β_I polymorph carbon coated by the xerogel process at a rate of 10 mA g^{-1}. The inset shows the performance of uncoated material. (b) Variation of discharge capacity with cycle number for the carbon-coated β_I polymorph cycled between 2.0 and 4.6 V at 10 mA g^{-1}.[32]

Li_2CoSiO_4

Lyness *et al.*[32] show that the three polymorphs of Li_2CoSiO_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, $LiCoPO_4$. For the β_I polymorph, coating the as-prepared material with carbon switches on electrochemistry without the need for ball-milling and gives superior charge capacity (170 mA h g^{-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 Li_2CoSiO_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 Li_2CoSiO_4/C composite materials, with a reported charge capacity of 234 mA h g^{-1}.

4. Conclusions and future outlook

This review has highlighted an important class of polyoxyanion compounds based on the orthosilicates, Li_2MSiO_4 (where M = Mn, Fe, and 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 $LiFePO_4$. The challenges have been discussed above and are summarised here.

(i) For all Li_2MSiO_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, nano-scale 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, and 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 mA h g^{-1}) are desirable, preferably with higher voltages such as those associated with Li_2MnSiO_4. Modifying the stoichiometric materials to enhance the Li composition range will be important.

(v) Most studies have concentrated on pure Li_2MSiO_4 compositions, which are a necessary prelude to studying solid solutions of Li_2MSiO_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.

Acknowledgements

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