# The lithium intercalation compound $Li_2CoSiO_4$ and its behaviour as a positive electrode for lithium batteries†

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**The electrochemical behaviour of 3 polymorphs of the lithium intercalation compound $Li_2CoSiO_4$, $\beta_I$, $\beta_{II}$ and $\gamma_0$, as positive electrodes in rechargeable lithium batteries is investigated for the first time.**

The layered Li intercalation compound, $LiCoO_2$, is used as the cathode in the majority of commercial rechargeable lithium-ion batteries.[1,2] Alternative compounds, such as $LiNiO_2$ or $LiMnO_2$ have also been considered; their solid solutions, *e.g.* $Li(Co_{1/3}Mn_{1/3}Ni_{1/3})O_2$ are used in the latest commercial products.[3–5] Recognition that compounds based on the phosphate anion, such as the olivine $LiFePO_4$, could act as lithium intercalation hosts, and could operate as cathodes in rechargeable lithium batteries, represented a significant breakthrough.[6] Bonding of the oxygen to the phosphorus stabilises the former with respect to evolution from the structure, an important problem on charging simple transition metal oxides. Recently, an entirely new class of lithium intercalation compounds based on silicates, $Li_2MSiO_4$, where M = Fe, Mn, has been described.[7] Of these the most studied is $Li_2FeSiO_4$, it has been shown that at 60 °C 165 mA h $g^{-1}$ of charge may be extracted, corresponding to one lithium per formula unit; with reversible lithium cycling over the range $Li_xFeSiO_4$, $1.15 < x < 2$, corresponding to 140 mA h $g^{-1}$ when suitably carbon coated and with a particle size of 150 nm.[7a] Si doped $LiCoO_2$ gave $Li_2CoSiO_4$ as an impurity with enhanced electrochemical properties but behaviour of the pure phase was not reported.[8] Here we present the first preliminary report on the electrochemistry of three polymorphs of the compound $Li_2CoSiO_4$.§

The $Li_2MSiO_4$ compounds (M = Fe, Mn, Co) belong to a family of materials known as the tetrahedral structures.[9] They 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.[10] The tetrahedral structures exhibit a rich polymorphism, with more than eight polymorphs known. They may be divided into two families, designated β and γ. In the case of the former all the tetrahedra point in the same direction, perpendicular to the close-packed planes, and share only corners with each other, whereas, 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. 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.[11] Several variants of both β and γ exist, involving either ordering or distortions of the parent structures, they are designated $\beta_I$, $\gamma_0$, $\gamma_{II}$, *etc.* In many cases these phases may be quenched to room temperature, where they exhibit long-term stability. Originally the different polymorphs were distinguished only on the basis of differences in their powder X-ray diffraction patterns.[9a] More recently, the complete crystal structures of a few isolated examples have been solved.[12]

$Li_2CoSiO_4$ compounds were synthesised by initial hydrothermal reaction which produces the $\beta_{II}$ polymorph. The $\beta_I$ form was obtained by heating the $\beta_{II}$ phase in air to 700 °C for 2 h. The $\gamma_0$ phase was formed by heating the $\beta_{II}$ polymorph to 1100 °C for 2 h, then lowering the temperature to 850 °C whereupon the material was quenched to room temperature. Powder X-ray diffraction patterns of as-prepared $Li_2CoSiO_4$, and those heated to 700 and 1100 °C are presented in Fig. 2 (Stoe STADI/P diffractometer, Fe-$K\alpha_1$). They correspond to the three polymorphs $\beta_{II}$, $\beta_I$ and $\gamma_0$, respectively. Their structures have been refined by the Rietveld method (TOPAS).[13] Full details are beyond the scope of this communication but will be reported later. The structures of $\beta_{II}$, $\beta_I$ and $\gamma_0$ are shown in Fig. 1.

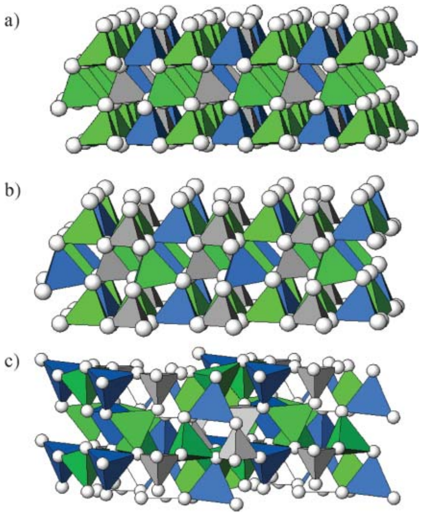

**Fig. 1** Crystal structures of three tetrahedral polymorphs of $Li_2MXO_4$: (a) $\beta_{II}$, (b) $\beta_I$, (c) $\gamma_0$. Grey tetrahedra: $XO_4$, blue: $MO_4$, green: $LiO_4$.

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† Electronic supplementary information (ESI) available: TEM images of composite cathodes. Comparison of powder X-ray diffraction patterns for as-prepared and ball-milled $\beta_I$, $\beta_{II}$ and $\gamma_0$ $Li_2CoSiO_4$. See DOI: 10.1039/b711552k

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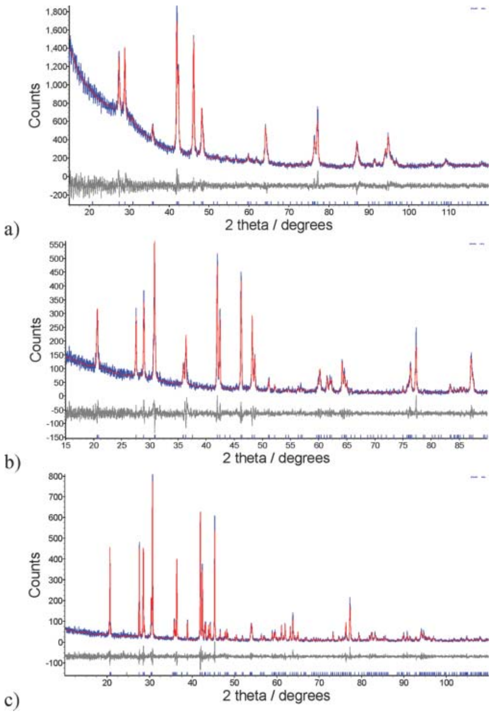

**Fig. 2** Fitted powder X-ray diffraction data for the three $Li_2CoSiO_4$ polymorphs: (a) $\beta_{II}$, (b) $\beta_I$, (c) $\gamma_0$.

The electrochemistry of all three polymorphs was investigated by forming composite electrodes as described in the notes. The capacity to extract lithium from the three polymorphs, even when charged slowly to 4.6 V, was very low. Each polymorph was mixed with Super P carbon in the ratio 8 : 2 and ball-milled (SPEX Centri-Prep 8000 M mixer/mill) for 1 h. TEM data collected after ball-milling (Jeol JEM-2011) indicated particle sizes of 50–100 nm for all three polymorphs and powder X-ray diffraction data showed peak-broadening compared with the as-prepared materials (see ESI†). Analysis of the peak widths using the Scherer formula revealed domain sizes of 10–40 nm. These are smaller than the particle sizes observed by TEM demonstrating that ball-milling introduces a domain structure/strain within the grains.

Ball-milling significantly improves the electrochemical response. Cells fabricated from the ball-milled polymorphs were subjected to charge and discharge at 50 °C, a typical temperature used for other $Li_2MSiO_4$ materials, Fig. 3.[7] The ball-milled $\beta_{II}$ phase exhibits a gentle increase in potential on the first charge, corresponding to extraction of 180 mA h $g^{-1}$ (equivalent to 1.1 Li per formula unit). Lithium removal is accompanied by oxidation of the tetrahedral $Co^{2+}$ to $Co^{3+}$. The first discharge capacity is much smaller at around 30 mA h $g^{-1}$. Subsequent cycling leads to further capacity fade, such that after 10 cycles the cell capacity is negligible. Turning to the $\beta_I$ polymorph, cycled under the same conditions, the shape of the first charge curve is similar, although with some additional structure evident. The first charge capacity is significantly lower at only 80 mA h $g^{-1}$. The discharge capacity on the first cycle was again around 30 mA h $g^{-1}$, although by virtue of the lower charge capacity the efficiency had improved from 14% for $\beta_{II}$ to 38% for $\beta_I$. Again after 10 cycles the capacity of the $\beta_I$ polymorph was negligible, Fig. 3(b). The $\gamma_0$ polymorph also exhibits a slow potential rise on the first charge corresponding to a capacity of 100 mA h $g^{-1}$ and around 30 mA h $g^{-1}$ on discharge, again with negligible capacity after 10 cycles.

Although the load curves in Fig. 3, despite a low rate of 10 mA $g^{-1}$, may still be somewhat influenced by kinetics, it is interesting to note that the charge and discharge potentials are all similar, suggesting that the structural differences in the three polymorphs are not sufficient to induce major changes in the $Li^+$ and $e^-$ chemical potentials. Also the values are in broad agreement with those predicted by DFT + U calculations for $Li_2CoSiO_4$ (4.4 V).[7d,e] They are higher than $Li_2FeSiO_4$ ($\sim$3 V) and $Li_2MnSiO_4$ ($\sim$4.2 V).

Although ball-milling aids the distribution of carbon within the composite electrode, carbon coating the particles would further improve the efficiency of the "wiring", as has been demonstrated for $LiFePO_4$.[14] It is necessary to pyrolyse the carbon precursors above 650 °C to form sufficient $sp^2$ linkages to promote good electron transport. All our attempts to carbon coat the ball-milled polymorphs using a variety of precursors *e.g.* sucrose, resulted in reduction of $Li_2CoSiO_4$ and the production of Co metal and $Li_2SiO_3$, as demonstrated by powder XRD. However, in the case of the $\beta_I$ polymorph, we were able to coat the as-prepared particles with carbon without such reduction occurring. The difference may reflect the greater reactivity of the particle surfaces formed during ball-milling, making them more susceptible to reduction. Success so far has been restricted to the $\beta_I$ polymorph because heating the $\beta_{II}$ polymorph at high enough temperatures to induce a conductive carbon coat results in conversion to $\beta_I$. In the case of the $\gamma_0$ phase, to date it has proved impossible to quench the sample sufficiently rapidly in an inert atmosphere to form a single $\gamma_0$ phase.

The "wiring" of $\beta_I$-$Li_2CoSiO_4$ was achieved using the resorcinol-formaldehyde approach.[15] Hydrothermally prepared $Li_2CoSiO_4$ was mixed with 15 wt% of dried carbon-gel (pre-pyrolysis xerogel) and heated to 700 °C under flowing argon for 2 h. Electrochemical results for composite electrodes fabricated using the $\beta_I$/carbon composite are shown in Fig. 4. A well defined plateau is observed at around 4.25 V on the first charge. Despite the higher polarisation at the start of charging compared with the ball-milled material, a

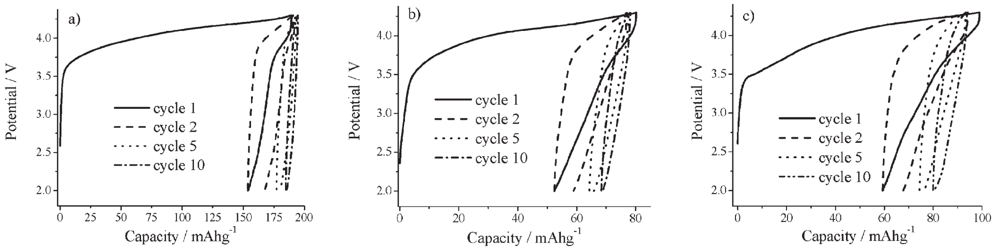

**Fig. 3** Variation of voltage with state of charge (Li content) on cycling the three $Li_2CoSiO_4$ polymorphs at a rate of 10 mA $g^{-1}$: (a) $\beta_{II}$, (b) $\beta_I$, (c) $\gamma_0$.

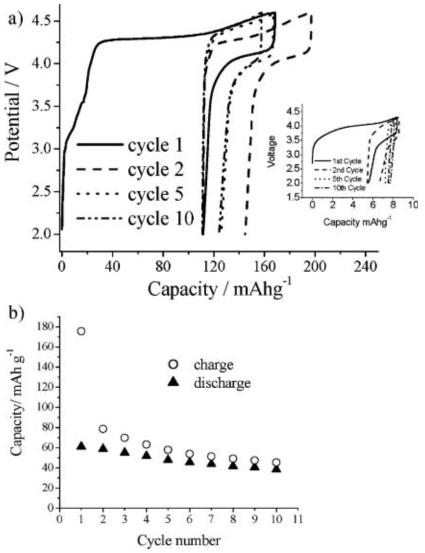

**Fig. 4** (a) Variation of voltage with state of charge (Li content) on cycling the $\beta_I$ $Li_2CoSiO_4$ polymorph carbon coated by the xerogel process at a rate of 10 mA g$^{-1}$. Inset shows performance of uncoated material. (b) Variation of discharge capacity with cycle number for the carbon-coated $\beta_I$ $Li_2CoSiO_4$ polymorph cycled between 2.0 and 4.6 V at 10 mA g$^{-1}$.

higher capacity of 95 mA h g$^{-1}$ is obtained to the same 4.3 V cut-off, compared with 80 mA h g$^{-1}$ for the ball-milled material. This highlights the effectiveness of the carbon coat in "wiring" the electrode and hence the crucial role of electron transport to the particles on the electrochemical performance. This is reinforced on recalling that the bulk particles, without carbon "wiring" demonstrated almost no electrochemical activity (see inset, Fig. 4). By extending the voltage cut-off to 4.6 V, 170 mA h g$^{-1}$, corresponding to 1.1 Li per formula unit, could be extracted. The first discharge capacity was also improved (60 mA h g$^{-1}$) compared with the as-prepared or the ball-milled materials. As is evident in Fig. 4(b) capacity retention is better than for any of the as-prepared or ball-milled materials, with a capacity of 40 mA h g$^{-1}$ observed after 10 cycles. The previous theoretical study suggested extraction of the second Li (associated with the $Co^{3+/4+}$ couple) would occur at $\sim$5 V, above the stability of the electrolyte and in agreement with the results here (*i.e.* only 1 Li extracted to 4.6 V).[7d]

In conclusion, the first preliminary results concerning the electrochemical performance of any $Li_2CoSiO_4$ materials with, attention focusing on the $\beta_I$, $\beta_{II}$ and $\gamma_0$ polymorphs, have all been presented. three exhibit electrochemical activity when ball-milled, although with severe capacity fading after a few cycles. In the case of the $\beta_I$ 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$^{-1}$ $\equiv$ 1.1 Li per formula unit) and cyclability, compared with the same phase when ball-milled with carbon. Only one Li could be extracted up to 4.6 V in agreement with theoretical predictions. For all polymorphs there is a significant difference between the first charge and subsequent cycling. Usually this is indicative of structural changes. Further work on these materials is underway, including investigating any such structural changes. This study has concentrated on the pure $Li_2CoSiO_4$ polymorphs, a necessary prelude to studying solid solutions of $Li_2MSiO_4$, M = Fe, Mn, Co. It will be interesting to see whether the performance of such solid solutions proves superior to the pure phases as observed in the case of the $LiMO_2$ cathodes *e.g.* $Li(Co_{1/3}Mn_{1/3}Ni_{1/3})O_2$ and therefore of technological significance.

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## Notes and references

§ *Hydrothermal synthesis* of $Li_2CoSiO_4$ : 0.05 mol. $LiOH{\cdot}H_2O$ (Aldrich), was added to 0.0125 mol $SiO_2$ (Aldrich) in 20 ml of distilled water and stirred. 0.0125 mol $CoCl_2$ (Aldrich) was added to 10 ml of ethylene glycol and stirred under gentle heat until dissolution occurred. The two solutions were then mixed with stirring and the slurry transferred to a 40 ml Teflon-lined autoclave. The remaining volume was topped up with distilled water. The sealed autoclave was heated at 150 °C for 72 h. The product was filtered off and dried at 60 °C overnight.

Composite electrodes consisted of the active material, super P carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in the ratio 75 : 18 : 7. Electrochemical cells consisted of the $Li_2CoSiO_4$ composite electrode, a lithium metal counter electrode and the electrolyte, a 1 molal solution of $LiPF_6$ in ethylene carbonate–dimethyl carbonate 1 : 1 (v/v (Merck)). All cells were constructed and handled in an Ar filled MBraun glovebox. Electrochemical measurements were carried out at 30 °C using a Maccor Series 4200 battery cycler.

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