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FEATURE ARTICLE

# Solid-state chemistry of lithium power sources†

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**This article describes the solid-state chemistry of intercalation compounds that underpins a revolutionary new rechargeable lithium battery which has recently achieved phenomenal commercial success. The battery can store more than twice the energy compared with conventional alternatives of the same size and mass and holds the key to the future improvement of consumer electronic products (*e.g.* mobile telephones), electric vehicles and implantable medical devices (*e.g.* the artificial heart). Attention is focused on those lithium intercalation compounds that are useful as positive electrodes in rechargeable lithium batteries. The basic operation of the cell is summarised briefly and the structure/property relationships are developed that are important for the solid-state chemist when attempting to design and synthesise new lithium intercalation compounds capable of operating as positive electrodes. Finally, the structure, electronic structure and intercalation chemistry of several important positive intercalation electrodes are discussed including some which show considerable promise for applications in future generations of rechargeable lithium batteries.**

## Introduction

Why should chemists be interested in rechargeable lithium batteries? For better or worse, chemical research must now find expression in its benefit to industrial competitiveness or the quality of life. This is not necessarily in conflict with its more timeless *raison d'être, i.e.* the advancement of knowledge. In many areas of chemistry it is possible, although often hard, to be interesting and useful at the same time. Some of the most exciting fundamental scientific developments in solid-state chemistry within the last decade, *e.g.* zeolites for catalysis, have occurred against a background of attempting to advance technology and reduce energy costs.

The overwhelming need for lightweight and compact sources of portable electricity has resulted in a massive international effort into the development of radically new rechargeable batteries. This has led recently to the first successful commercialisation of a rechargeable lithium battery.[1,2] The device is a triumph of solid-state chemistry and electrochemistry; the relevance of electrochemistry to lithium batteries is obvious, however if it were not for crucial advances in the solid-state chemistry of intercalation solids, rechargeable lithium batteries would not have achieved the success that they have. In this article I aim to highlight the key challenge presented to the solid-state chemist, namely, the development of new intercalation compounds as positive electrodes for rechargeable lithium batteries.

## Rechargeable lithium batteries

The considerable technological impetus in this area comes from three main sources, consumer electronics (*e.g.* mobile telephones), electric vehicles and implantable medical devices (*e.g.* the artificial heart).

The introduction by Sony in 1990 of the world's first commercially successful rechargeable lithium battery represented a revolution in the power source industry.[1–3] It has been likened by some to the semiconductor revolution which saw the replacement of the valve by the transistor in the 1940s and 50s. The new cell can store more than twice the energy compared with conventional rechargeable batteries of the same size and mass, an achievement which is remarkable in an industry that traditionally measures improvements in a few percentage points. The Sony cell represents but a first step on the road to greatly improved sources of portable electrical power, there is much scope and indeed need for further development.[2]

The essential elements of the Sony cell are shown schematically in Fig. 1(*a*). The cell is constructed in the discharged state and consists of a positive electrode composed of a thin layer of powdered $LiCoO_2$ mounted on aluminium foil, a negative electrode formed from a thin layer of powdered graphite, or certain other carbons, mounted on a copper foil. The two electrodes are separated by a porous plastic film soaked typically in $LiPF_6$ dissolved in a mixture of dimethyl carbonate and ethylene carbonate. Charging the cell involves diffusion of lithium ions within the $LiCoO_2$ particles towards their interface with the electrolyte, the lithium ions then cross the electrolyte and are intercalated between the carbon layers in the graphite electrode. Charge balance requires that the equivalent number of electrons must pass around the external circuit. Discharge reverses the process moving lithium out of the graphite and reforming $LiCoO_2$. This cell may be contrasted with earlier designs which employed lithium metal rather than graphite as the negative electrode, Fig. 1(*b*). The reactivity of lithium metal and the difficulty of plating and stripping it with high efficiency, have resulted in concerns over safety and the performance of this design. The Sony cell, which is known variously as a rocking-chair, swing or LION cell, to distinguish it from the lithium metal design, is a true expression of solid-state intercalation chemistry involving, as it does, the flow of lithium

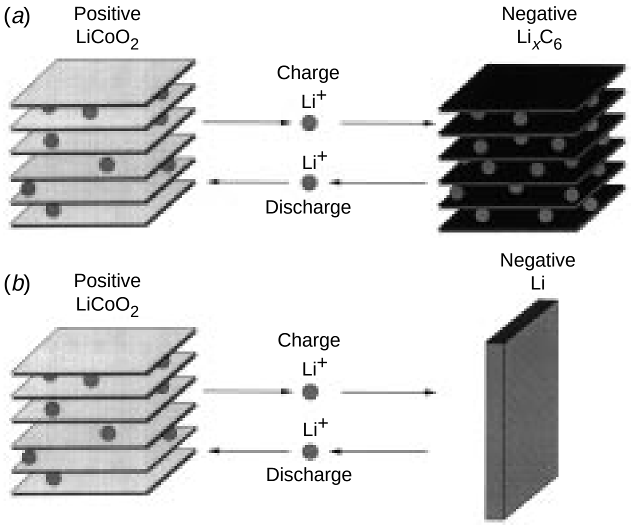

**Fig. 1** Schematic representation of (*a*) the Sony rocking-chair cell and (*b*) a rechargeable lithium cell with a lithium metal negative electrode. The maximum lithium content in ordered graphite is $LiC_6$.

ions between two intercalation hosts. The performance advantage over more conventional rechargeable batteries such as nickel–cadmium lies largely in the voltage. The Sony cell has an average potential of 3.6 V which is almost three times that of nickel–cadmium so that three conventional cells can be replaced by only one lithium cell![1,3]

A number of reviews have appeared which deal with rechargeable lithium batteries including graphite and other carbon-based negative electrodes.[4–7] Although the Sony cell currently uses a liquid electrolyte, the future will see replacement of this by a solid polymer leading to all-solid-state rechargeable lithium batteries.[8]

## Relating solid-state chemistry to positive intercalation electrodes

For our purposes, intercalation or insertion solids may be defined as hosts into which atoms (or more commonly ions + electrons) may be inserted or removed without a major disruption of the structure.[9–12] Molecular intercalation has been reviewed by O'Hare.[13]

In order to use our knowledge of solid-state chemistry to design and synthesise new intercalation compounds that will exhibit improved performance as positive electrodes for new generations of rechargeable lithium batteries, we must first understand what properties the intercalation solid should possess and how this relates to the structure and composition of the solid. The key structure/property relationships are listed in Table 1. As can be seen, a single compound must possess fourteen, often quite distinct, attributes and this serves to illustrate how challenging it is to develop solids which will be technologically competitive! Let us consider some of these attributes and their relationship to the solid-state chemistry in more detail.

Firstly, positive electrodes must be intercalation compounds; only such compounds avoid the large kinetic barriers of defect diffusion and nucleation and growth associated with the majority of solid-state reactions. Also, as prepared, they should contain lithium, *i.e.* be in the fully discharged state since rocking chair cells are assembled in this state.

The voltage of the cell is a crucial parameter and this should be large. If we consider a rocking-chair cell, such as graphite/$LiCoO_2$, then the voltage between the two electrodes is related to the work the cell can deliver on transferring electrons around an external circuit and to the free energy change on transferring lithium from one intercalation electrode to the other. The free energy change associated with the transfer of one mole of lithium between the two intercalation electrodes is equivalent to the difference in the chemical potential of lithium in the two electrodes [eqn. (1)],[14,15]

$$V = -\frac{(\mu_{\mathrm{Li}}^{\mathrm{int}} - \mu_{\mathrm{Li}}^{\mathrm{graph}})}{nF} \qquad (1)$$

where $V$ is the open circuit voltage of the cell, $\mu_{\mathrm{Li}}^{\mathrm{int}}$ and $\mu_{\mathrm{Li}}^{\mathrm{graph}}$ the chemical potentials of lithium in the positive intercalation and graphite electrodes respectively, $n = 1$ (since one $e^-$ is transferred for each lithium) and $F$ is Faraday's constant. On discharge, lithium is transferred from a state of high $\mu_{\mathrm{Li}}^{\mathrm{graph}}$ (high energy) in the negative graphite electrode to one of low $\mu_{\mathrm{Li}}^{\mathrm{int}}$ (low energy) in the positive intercalation electrode; as a result work can be done by the cell. According to eqn. (1), in order to ensure a large cell voltage we must select positive intercalation electrodes which possess a low $\mu_{\mathrm{Li}}^{\mathrm{int}}$. On discharging a rocking-chair cell the lithium content and hence chemical potential and voltage, will change in each electrode ($\mu_{\mathrm{Li}} = \mu_{\mathrm{Li}}^{\mathrm{o}} + RT\ln a$, where $a$ is the activity of lithium). It is convenient and normal practice therefore to measure the potential of a positive intercalation electrode against lithium metal (which has an invariant $\mu_{\mathrm{Li}}$) and to use the latter's chemical potential as the standard state for lithium in the positive electrode. Lithium is rarely in the form of Li atoms in the intercalation compounds of interest here but instead exists as $Li^+$ ions along with their charge-compensating electrons, the latter located in the d levels of the transition-metal ion. As a result, it is helpful when considering structure–property relationships to separate $\mu_{\mathrm{Li}}^{\mathrm{int}}$ according to eqn. (2)

$$\mu_{\mathrm{Li}}^{\mathrm{int}} = \mu_{\mathrm{Li^+}}^{\mathrm{int}} + \mu_{\mathrm{e^-}}^{\mathrm{int}} \qquad (2)$$

where $\mu_{\mathrm{Li^+}}^{\mathrm{int}}$ and $\mu_{\mathrm{e^-}}^{\mathrm{nt}}$ represent respectively the chemical potentials of $Li^+$ ions and electrons.‡ The ion and electron chemical potentials include both energy and entropy terms. In developing the gross structure–property relationships the entropy terms may be neglected since over most of the composition range they are small, vary little and make a similar contribution to each intercalation compound. The entropy of electrons in a band is negligible.

**Table 1** Criteria for intercalation compounds as positive electrodes

| | |
|---|---|
| 1 | Must be an intercalation host for lithium |
| 2 | Low Fermi level and $Li^+$ site energy → high open-circuit voltage |
| 3 | Electrode potential varies little with lithium content → cell voltage varies little with state of charge |
| 4 | Capable of accommodating large quantities of lithium per formula unit → high capacity |
| 5 | Low formula mass → high gravimetric energy density |
| 6 | Low molar volume → high volumetric energy density |
| 7 | Sustain high rates of lithium intercalation and deintercalation → high cell discharge/charge rates |
| 8 | Highly reversible lithium intercalation → many charge–discharge cycles |
| 9 | Avoid co-intercalation of solvent |
| 10 | Stable in contact with candidate electrolytes |
| 11 | Adequate electronic conductivity |
| 12 | Low cost |
| 13 | Easily fabricated into electrode |
| 14 | Evironmentally friendly |

This torrid trip through some simple thermodynamics has brought us to the conclusion, important for the solid-state chemist, that the potential of a positive intercalation electrode, and hence the voltage of the cell, will depend on the energy of the electrons and the $Li^+$ ions in the host. On inserting electrons into an intercalation host they will enter at the Fermi level, $E_F$ and this is the electron energy of importance [eqn. (3)].§¶

$$\mathrm{E_F} = \mu_{\mathrm{e}} \qquad (3)$$

The site energy for $Li^+$ is the major factor determining the ion contribution to the overall energy. Mutual repulsion between the $Li^+$ ions is usually of secondary importance. Hence maximising the positive electrode potential reduces to designing intercalation compounds with a low Fermi level and a high stability (low energy) for $Li^+$ in its sites. It is important to note that the electrode potential of graphite or other carbon electrodes is some +10 to +800 mV *vs.* lithium, therefore for rocking chair cells we must select intercalation electrodes with somewhat larger positive potentials (*i.e.* lower Li chemical potentials) than is necessary for cells with lithium metal electrodes.

Let us consider further the problem of engineering a low Fermi level. The lowest Fermi level which can be achieved for an intercalation compound is determined by the energy corresponding to the top of the valence band. In oxides the valence band is largely of oxygen 2p parentage and lies significantly below the top of the 3p valence band in the corresponding sulphides. As a result, Fermi levels in oxides can be more than 2 eV lower, resulting in potentials of between 4 and 5 V *vs.* the $Li^+$/Li couple. Therefore, the focus is on oxides rather than chalcogenides. For any given transition-metal oxide the Fermi level is set by the position of the cation d levels. The lowest d levels are associated with those ions from the centre or right of the first transition series, *i.e.* Cr, Fe, Mn, Co, Ni; these all exhibit +4 oxidation states corresponding to d levels which lie close to (usually just above) the top of the oxygen valence band. $Li_{1-x}Cr_2O_4$, for example, when combined with a lithium negative electrode gives an open circuit potential of 5 V associated with the $Cr^{4+/3+}$ mixed-valence state.[17]

As lithium is inserted into the intercalation host forming a continuous range of solid solutions, the electrons fill up the band while the mutual repulsions between the $Li^+$ ions rises. The net effect is that the potential will decrease somewhat with increasing Li content; whereas in many systems it turns out that this can be rationalised entirely by considering only the ion repulsions,[14] in some cases both ion and electron interactions are important.[18] If, on the other hand, intercalation induces the formation of a new phase and both phases have fixed composition then insertion is simply accompanied by the conversion of one phase to the other. This in turn is associated with a constant change of chemical potential and therefore a constant voltage as a function of the degree of intercalation (state-of-charge).

Before leaving the topic of electrode potentials it is worth noting that the relationship between the cell voltage and the lithium chemical potentials in the electrodes can be derived in another way which serves to highlight a frequently misunderstood fact. It is often stated that the voltage of a cell is determined by the difference between the Fermi levels of the two electrodes, this is incorrect. The voltage is equal to the difference in the Fermi levels between the electrodes only when they are in a cell *i.e.* in mutual contact with an electrolyte. Such Fermi levels are not those of the isolated electrodes. Selecting a lithium intercalation electrode based on its Fermi level will not yield the desired cell voltage.‖

One of the most important factors governing the performance of a cell is the energy which can be stored per unit weight and volume, *i.e.* the gravimetric and volumetric energy density. For electric vehicles, batteries are required which provide a high gravimetric energy density whereas for implantable medical devices volumetric energy is more important. Since energy is stored in the form of lithium in the intercalation electrodes the gravimetric and volumetric energy density of the positive electrode is of great importance and is given by eqn. (4),

$$E = V_e Q \qquad (4)$$

where $E$ is the volumetric or gravimetric energy density, $V_e$ is the electrode potential and $Q$ is the charge stored per unit mass or volume of the intercalation compound. Energy densities are conventionally expressed in terms of W h $kg^{-1}$ or W h $l^{-1}$ whereas $Q$ is expressed in terms of mA h $g^{-1}$ or A h $l^{-1}$. The energy density depends therefore on two separate factors, the electrode potential and the charge. Potential has been dealt with above. The charge stored is equivalent to the amount of lithium that can be accommodated within the intercalation host. It is important for the solid-state chemist to design intercalation hosts which can reversibly insert a large amount of lithium per formula unit. If the capacity to store lithium is high, then a high gravimetric energy density will be assured provided the molar mass of the intercalation host is small. A high volumetric energy density will be obtained provided the molar volume is small. We see again that oxides will be preferable to chalcogenides in order to achieve a high gravimetric energy density and that we wish to choose intercalation hosts that contain the active redox couple and little else. Considering both $V_e$ and $Q$, a metal oxide of the formula $LiMO_2$ from which all the lithium may be reversibly deintercalated and in which M is a light element, in a high oxidation state ($M^{4+/3+}$ couple) and with a close-packed structure would seem to be optimal. It is no coincidence that the positive electrode in the Sony cell is $LiCoO_2$.

The rate at which a cell can be discharged or charged is an important parameter and is limited by the rate of lithium intercalation or deintercalation. Electroneutrality demands that the magnitude of the flux of $Li^+$ ions and their charge compensating electrons into and out from the host must be the same. It is the coupled diffusion of $Li^+$ and electrons down a concentration gradient that is important, rather than the individual diffusivities (mobilities) of the ions and electrons alone. A coupled diffusion coefficient may be defined, it is generally known as the chemical diffusion coefficient, $\tilde{D}_{Li}$, and is a measure of the intrinsic rate capability of the electrode.

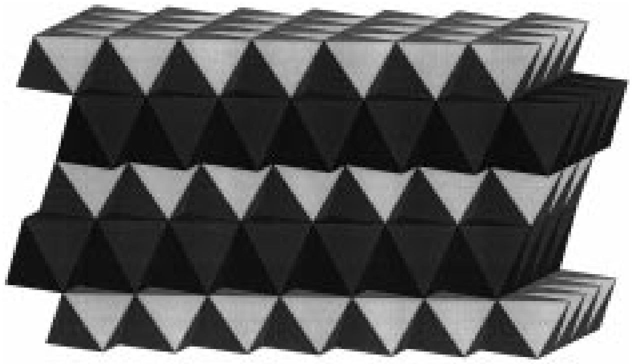

**Fig. 2** The crystal structure of $LiCoO_2$ or $LiNiO_2$. Dark and light octahedra represent respectively the sites for the transition-metal and lithium ions.

Several other factors are also of crucial importance. The chosen electrode must be stable in contact with the electrolyte of the cell. The surfaces of transition-metal oxides provide an ideal environment for catalytic decomposition of many electrolytes and this can present problems. Indeed metal oxide electrodes are frequently used for electrocatalysis in other applications! The starting materials used to prepare the intercalation electrode should be of low cost as should the preparation method. However, above all, the intercalation electrode must be environmentally benign.

## Intercalation electrodes

Many intercalation compounds have been studied as possible positive electrodes for rechargeable lithium batteries. Limitations of space demands that attention is concentrated on the three compounds of main interest. The author apologises to those whose work could not be included.

### *$LiCoO_2$ and $LiNiO_2$*[19–21]

The structures of $LiCoO_2$ and $LiNiO_2$ are identical and shown in Fig. 2. The oxide ions adopt a cubic close-packed arrangement with $Co^{3+}$ or $Ni^{3+}$ ions occupying octahedral sites between adjacent oxide ion layers. Only alternate sheets of octahedral sites are occupied by the transition metal ions with the remaining sheets being occupied by $Li^+$. The structure is slightly distorted giving rise to rhombohedral symmetry, space group $R\bar{3}m$.

The electronic structure of intercalation electrodes is an important factor which as we have seen has a strong influence on the voltage and can also induce structured distortions. Too little attention has been paid to the rôle of electronic structure in the past. The electronic structure of $LiCoO_2$ may be derived as follows. $Co^{3+}$ ($3d^6$) adopts a low-spin configuration ($t_{2g}{}^6e_g{}^0$) in an octahedral oxygen environment. The $t_{2g}$ orbitals are energetically close to the oxygen 2p orbitals and those 2p orbitals of $\pi$ symmetry will overlap strongly with the Co $t_{2g}$ orbitals. As a result there is considerable covalent mixing and consequently a high degree of delocalisation over the $CoO_6$ octahedra. The Co–O–Co angle is close to 90° and hence neighbouring cobalt ions overlap with mutually orthogonal 2p orbitals on the bridging oxygens. This inhibits long-range Co–O–Co interactions, thus attenuating band formation due to metal–oxygen interactions. Spectroscopic data suggests that the electronic structure of $LiCoO_2$ more closely approximates to a localised Co($3d^6$) electronic configuration than to a band. Full occupancy of the $t_{2g}$ $\pi^*$ orbitals which are separated energetically from the $e_g$ $\sigma^*$ orbitals ensures semiconductor behaviour for $LiCoO_2$. The extraction of lithium from between the oxide ion layers is facile and a chemical diffusion coefficient for the

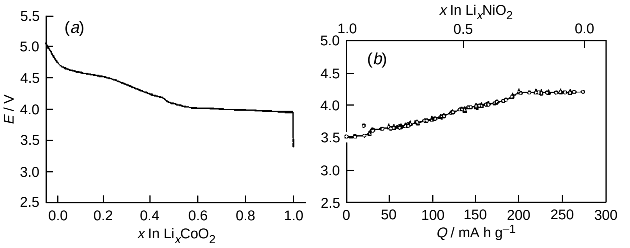

**Fig. 3** Open-circuit voltage *vs*. $Li^+/Li$ couple as a function of lithium content in (*a*) $Li_xCoO_2$, reproduced from ref. 28 and (*b*) $Li_xNiO_2$, based on a figure presented in ref. 29. With the permission of The Electrochemical Society.

coupled ($Li^+ + e^-$) diffusion of $5 \times 10^{-8}$ cm$^2$ s$^{-1}$ at $Li_{0.65}CoO_2$ has been measured.[22] Such extraction is accompanied by oxidation of $Co^{3+}$ to $Co^{4+}$ (low-spin $d^5$). The associated contraction of the *a* axis of the unit cell (which lies in the oxide layers) signals a shorter Co···Co distance, reduced from 2.83 Å in the case of $LiCoO_2$ to 2.81 Å for $Li_{0.9}CoO_2$. The strongly covalent Co–O interactions, will, due to the nephaluxetic effect, produce expanded antibonding d orbitals. Together the orbital expansion and shorter Co···Co distance conspire to make possible direct overlap of cobalt $t_{2g}$ orbitals across a shared octahedral edge resulting in a narrow d band and hole conduction in the mixed valence $Co^{4+/3+}$ system. The critical Co···Co distance for direct $t_{2g}$–$t_{2g}$ interactions is 2.82 Å, consistent with the switch from insulator to metallic behaviour on extracting a relatively small amount (10%) of lithium from $LiCoO_2$. Experimental evidence verifies that extraction of small quantities of lithium from $LiCoO_2$ does indeed induce metallic behaviour.[23] Of course we cannot rule out the possibility of $Co^{4+}$ d levels being located just below the top of the oxygen 2p band and introducing holes in it which would also lead to metallic behaviour; further studies are required to resolve this. In any case the low lying $Co^{4+/3+}$ couple gives rise to a high potential of $>4$ V *vs*. the $Li^+/Li$ couple, Fig. 3.

$LiNiO_2$ adopts a low-spin $d^7$ configuration with fully occupied $t_{2g}$ levels and one electron in the $e_g$ orbitals. Full occupancy of the $t_{2g}$ levels implies that we must focus our attention on the single electron in the $e_g$ orbitals to understand the conduction process. The $e_g$ orbitals will overlap with oxygen 2p orbitals of σ symmetry giving rise to strong interactions but again neighbouring nickel ions form a 90° Ni–O–Ni geometry and therefore overlap is with mutually orthogonal 2p orbitals on the bridging oxygen. This inhibits delocalisation extending beyond the $NiO_6$ octahedron and again attenuates band formation. As a result the $e_g$ electron remains in a localised atomic orbital on nickel although these are strongly antibonding associated with significant Ni–O covalency. A localised low-spin $d^7$ configuration is Jahn–Teller active. There is some evidence for a dynamic Jahn–Teller distortion from EXAFS studies but no cooperative, static, distortion of the structure has been detected.[24] Deintercalation is again facile with the chemical diffusion coefficient for Li reaching a maximum of $2 \times 10^{-7}$ cm$^2$ s$^{-1}$, amongst the highest observed in such materials.[25] Extraction of lithium is associated with oxidation of $Ni^{3+}$ to $Ni^{4+}$. Since the $e_g$ orbitals point towards the coordinating oxygens there is little opportunity for direct nickel–nickel interaction in contrast to the situation with the $t_{2g}$ orbitals in the cobalt compound. As a result, measurements of electronic transport on $Li_xNiO_2$ exhibit a small but definable activation energy for electronic transport associated with small polaron hopping in the mixed-valence $Ni^{4+/3+}$ state.[26] The location of the Fermi level in the higher energy $e_g$ orbitals, compared with the lower energy $t_{2g}$ orbitals in the analagous cobalt compound, results in an average voltage several hundred mV lower for $Li_xNiO_2$, Fig. 3(*b*).[19,27,28]

Considering now the structural changes that accompany lithium deintercalation from $LiCoO_2$ in more detail; this process does not correspond to a simple continuous solid solution as was first believed, instead several minor structural transformations occur.[28] Within the composition range $0.9 < x < 1$ in $Li_xCoO_2$, a single hexagonal phase exists, whereas within the range $0.78 < x < 0.9$, two hexagonal phases coexist giving way to a region, $0.51 < x < 0.78$, within which the second hexagonal phase exists alone. On further removal of lithium a monoclinic distortion of this second phase is observed for compositions in the narrow range $0.46 < x < 0.51$. Extraction of lithium from $x = 1$ to $x = 0.5$ is accompanied by an expansion in the *c* lattice parameter from approximately 14.1 to 14.5 Å. The loss of lithium from between the otherwise weakly van der Waals' bonded oxide layers is the origin of this expansion. Decrease in the *a* lattice parameter associated with oxidation of $Co^{3+}$ to the smaller $Co^{4+}$ has been highlighted above. Further deintercalation below $x = 0.46$ results in reversion to a hexagonal phase until the composition $Li_{0.22}CoO_2$ is reached whereupon a second monoclinic phase appears coexisting with the hexagonal phase until the composition $Li_{0.18}CoO_2$ is obtained, at which point the monoclinic phase exists alone. Below $x = 0.15$ another hexagonal phase appears corresponding to the fully delithiated $CoO_2$.[28] The monoclinic distortion at around $x = 0.5$ has been ascribed to lithium ordering,[27] however a complete rationale for the structural phase changes which occur on deintercalation has not yet been presented; nevertheless, there is no doubting the complexity of the structural chemistry. Until the recent studies by Amatucci, Tarascon and Klein,[28] it had been generally believed that the weak van der Waals' bonding exhibited by adjacent oxide ion layers would result in instability for a layered $CoO_2$ compound. These authors have shown this to be incorrect and have demonstrated that the structure of $CoO_2$ is not based on cubic close-packing but hexagonal close-packing ($CdI_2$ structure). This is the same structure commonly adopted by the layered chalogenides, *e.g.* $TiS_2$.[28] Two factors may play a rôle in stabilising $CoO_2$ with adjacent oxide layers. First, the low-lying $d^5$ configuration of $Co^{4+}$ ensures very significant covalent mixing with the neighbouring oxygen 2p orbitals resulting in a high degree of delocalisation. It is not therefore realistic to view the compound as possessing adjacent $O^{2-}$ layers. Second, as proposed before, a cooperative displacement of the $Co^{4+}$ ions results in a ferroelectric distortion establishing dipoles which will oppose the repulsive interactions between the oxide ion layers thus assisting stabilisation of the structure.[22]

The structural chemistry of $Li_xNiO_2$ is also complex.[27,29,30] Solid solutions with rhombohedral symmetry exist within the composition ranges $0.85 < x < 1$ and $0.32 < x < 0.43$. Between $x = 0.50$ and 0.75 a single monoclinic phase is observed. Over the range $x = 0$–0.32 a mixture of two rhombohedral phases is evident, one of these being $NiO_2$. Two-phase mixtures are also observed between each of the other single-phase ranges. The monoclinic distortion is believed to be associated with a superlattice arising from the ordering of lithium ions.[24,27,29] Arguments similar to those used for $CoO_2$ may be employed to explain the stability of $NiO_2$ particularly the high degree of Ni–O covalency. It is interesting to note that $NiO_2$ retains the cubic close packed structure of $LiNiO_2$ (*i.e.* the $CdCl_2$ structure type).[29]

In contrast to $LiCoO_2$, $LiNiO_2$ has proved impossible to prepare as a stoichiometric material. Instead compounds with the formula $Li_{1-\delta}Ni_{1+\delta}O_2$ are obtained. The closest approach to stoichiometry that has been possible so far corresponds to a δ of approximately 0.02 and may be prepared by reacting $Li_2O_2$ with NiO in oxygen at 700 °C.[31] Non-stoichiometry is associated with lithium deficiency and the presence of $Ni^{2+}$ ions in the lithium layers. These nickel ions serve to pin the oxide layers together reducing the mobility of the lithium ions, however compounds approaching the stoichiometric composition do exhibit a similar *c* lattice expansion on deintercalation to that observed for $LiCoO_2$. There is evidence that at high degrees of deintercalation further nickel ions may migrate from the Ni to the Li layers. Work by Delmas *et al.* has shown that the quantity of lithium extracted on first charging lithium nickel oxide cannot be reinserted.[24] In fact these authors claim that the capacity loss on the first cycle is a more significant factor than any loss of capacity due to continuous disordering of nickel on extended cycling. Even for relatively stoichiometric materials, reintercalation up to the composition $Li_{0.85}NiO_2$ is easy but beyond this limit proves very difficult. The mechanism they propose to explain this capacity loss is based on oxidation of the nickel ions in the lithium layers at high degrees of deintercalation, subsequent structural collapse around the $Ni^{3+}$ ions and the relatively high charge of these ions mitigates against $Li^+$ ions reoccupying the sites around nickel. The best electrochemical performance is obtained from materials that are as close as possible to the stoichiometric composition.

Comparing the properties of the $LiCoO_2$ and $LiNiO_2$ compounds as positive electrodes for rechargeable lithium batteries, both exhibit high voltages and facile lithium diffusion rates despite the complex structural changes. The fact that these structural changes are small and in some cases, at least, only associated with lithum ordering, explains the preservation of fast cycling kinetics. Complete removal of lithium from $LiNiO_2$ corresponds to a charge storage capacity of 275 mA h $g^{-1}$. In practical cells based on liquid electrolytes cycling can occur over the approximate composition range $0.3 < x < 0.9$ corresponding to 150–160 mA h $g^{-1}$ depending on the rate of charge/discharge. In the case of $LiCoO_2$, deintercalation to $Li_{0.5}CoO_2$ is possible with almost complete reinsertion of lithium, corresponding to a more modest 130 mA h $g^{-1}$ but at a slightly higher potential than the nickel electrode. As we now know the limits of deintercalation for this compound are not imposed by structural collapse *per se* but by the instability of the highly charged, and therefore high voltage, oxide in contact with the liquid electrolytes used in the commercial cells.[21] It is the somewhat more modest voltage of $LiNiO_2$ which gives rise to the greater capacity. $LiNiO_2$ is also attractive because it is cheaper than the cobalt alternative. However, $LiCoO_2$ has the significant advantage that it is easier to synthesise as a highly stoichiometric material and its structure is robust with respect to cycling, at least over the limited composition range stated above, with no evidence for cobalt disordering into the lithium layers. It is this that led to its selection by Sony for the first generation rechargeable lithium batteries.

### *Li(NiAl)O$_2$ and Li(NiCo)O$_2$*

In an attempt to improve on the properties of $LiNiO_2$ and take advantage of the lower cost of this material, partial substitution of nickel by other ions has been investigated. The work of Ohzuku *et al*. has shown that $LiAl_{0.25}Ni_{0.75}O_2$ can deliver a capacity of *ca*. 150 mA h $g^{-1}$ and with excellent capacity retention on cycling.[32] A complete range of solid solutions $Li(Ni_{1-y}Co_y)O_2$ may be prepared. It has been shown that partial replacement of Ni by Co yields a material which is cheaper than $LiCoO_2$ but with many of its advantages.[33] This solid solution will be used in future commercial rocking chair cells.

### *LiMn$_2$O$_4$ and related spinels*

Manganese is approximately 1% of the cost of cobalt and significantly more environmentally benign than either cobalt or nickel. These are major advantages and explain the intense interest in developing manganese oxide based positive electrodes. The use of $LiMn_2O_4$ spinels as positive electrode materials was first reported in 1983.[34–36] The attractive features of $LiMn_2O_4$ led in 1996 to the announcement by Nippon Moli, Japan of the first commercial rechargeable lithium battery in which $LiCoO_2$ is replaced by the lithium manganese oxide spinel.[37]

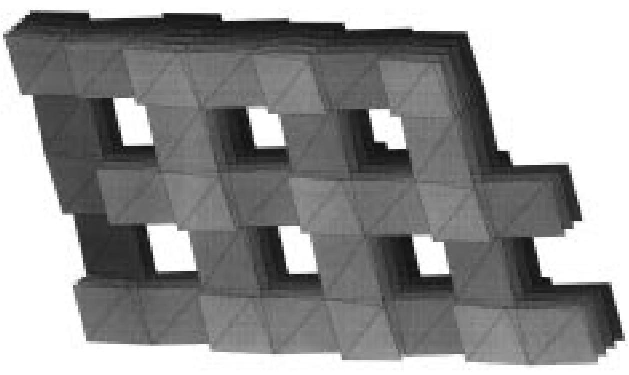

**Fig. 4** The $Mn_2O_4$ framework of the $LiMn_2O_4$ spinel consisting of a three-dimensional network of $MnO_6$ octahedra

$LiMn_2O_4$ is quite distinct from the layered oxides mentioned above in that it is a three-dimensional host. The spinel structure (space group $Fd\overline{3}m$) consists of cubic close-packed oxide ions with Mn ions in one half of the octahedral sites and $Li^+$ in one eighth of the tetrahedral sights within the cubic close-packed oxide array.[34,36] The $Mn_2O_4$ framework of the spinel structure is highly stable, Fig. 4, and defines a series of tunnels formed by the face-sharing of tetrahedral lithium (8a) and empty octahedral (16c) sites. These tunnels intersect in three dimensions and support rapid lithium diffusion, but unlike the layered compounds the spinels, because of their greater structural rigidity, are selective for lithium ions over solvent molecules or other larger cations (*i.e.* deleterious effects of solvent co-intercalation are avoided). Half of the octahedrally coordinated manganese ions are $Mn^{3+}$ (high-spin $3d^4$, $t_{2g}{}^3e_g{}^1$) and half $Mn^{4+}$ ($3d^3$, $t_{2g}{}^3$). Neighbouring Mn ions form 90° Mn–O–Mn interactions ensuring that the $t_{2g}$ and $e_g$ orbitals on adjacent Mn ions interact with mutually orthogonal oxygen 2p orbitals on the bridging oxygens, inhibiting band formation. The $t_{2g}$ orbitals are too contracted to overlap directly across a shared octahedral edge. As a result the d electrons are localised. Half the Mn sites are occupied by the Jahn–Teller active $Mn^{3+}$ ions and this is insufficient to promote a cooperative Jahn–Teller distortion until just below room temperature, the crystal structure at and above room temperature remains cubic. Electronic transport will occur by thermally activated small polaron hopping of the $e_g$ electron between neighbouring $Mn^{3+}/Mn^{4+}$ ions, the polaron is magnified by a dynamic Jahn–Teller distortion which must follow the electron. $LiMn_2O_4$ is a remarkable material. Li may be extracted yielding, when fully deintercalated, a polymorph of $MnO_2(MnO_2\text{-}\lambda)$ which cannot be prepared by other means. This is an excellent example of the rational synthesis of a target compound by *chimie douce* (soft chemistry).[38] Such deintercalation is associated with a potential of 4 V *vs*. $Li^+/Li$, Fig. 5. Lithium may also be intercalated into $LiMn_2O_4$ up to a maximum composition $Li_2Mn_2O_4$.[34,36] This is associated with the insertion of lithium into the octahedral (16c) sites and a potential of 3 V *vs*. $Li^+/Li$. The origin of this large voltage difference between lithium removal and insertion is believed to be related to the difference in the site energy of $Li^+$ in the tetrahedral (8a) and octahedral (16c) positions and its influence on the $\mu_{\mathrm{Li^+}}^{\mathrm{int}}$ and hence the potential [eqns. (1) and (2)]. In both cases the redox couple is $Mn^{4+/3+}$.

Let us consider the important intercalation chemistry of $LiMn_2O_4$ in more detail beginning with $Li_xMn_2O_4$ where $1 < x < 2$. Although this is a 3 V process and of limited interest in the context of rocking-chair cells it is of considerable importance for cells employing lithium metal negative electrodes. The gravimetric energy density of lithium is 3860 mA h $g^{-1}$, more than ten times that of graphite (372 mA h $g^{-1}$). For this reason, particularly in the context of developing batteries for electric vehicles, lithium metal systems continue to be intensively studied, although key problems connected with lithium cycling and safety remain to be solved. On inserting lithium into the octahedral (16c) sites of $Li_xMn_2O_4$ ($x = 1$), the $Mn^{4+}$ ions are reduced to $Mn^{3+}$ and a continuous solid solution is obtained up

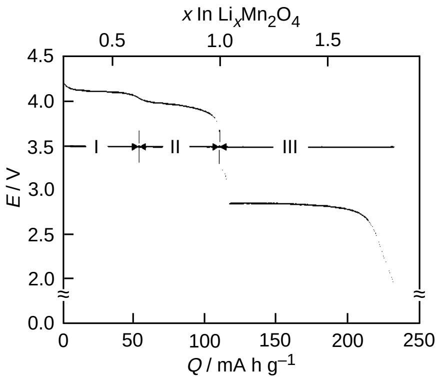

**Fig. 5** Open-circuit voltage *vs.* Li$^+$/Li couple as a function of lithium content in Li$_x$Mn$_2$O$_4$. Reproduced with permission from Ohzuku, Kitagowa and Hiral, *J. Electrochem. Soc.*, 1990, **17**, 769.

to $x = 1.1$. At this composition the Jahn–Teller active Mn$^{3+}$ ions are present in sufficient concentration to promote a cooperative distortion of the octahedral sites to tetragonal symmetry. Associated with this the cubic crystal symmetry of LiMn$_2$O$_4$ is lowered to tetragonal.[34,36] For $1.1 < x < 2$ a mixture of the cubic and tetragonal spinels coexist and intercalation involves the continuous conversion, within each particle, of the former phase to the latter. As a result the voltage does not vary with the lithium content in this composition range. Although the phase change is displacive and appears to be quite facile as judged by the rate of lithium insertion and removal, the abrupt change in unit-cell volume (6.5%) which accompanies the cubic-to-tetragonal phase transition in the spinel has a deleterious effect on the cyclability. Only tetragonal Li$_2$Mn$_2$O$_4$ should be present at the end of each discharge; however we have shown by X-ray diffraction carried out as a function of cycling that cubic LiMn$_2$O$_4$ accumulates at the end of discharge and that this is the primary cause of the significant loss of capacity to store lithium observed on cycling the spinel electrodes, Fig. 6.[39,40] The capacity loss arises because the particles contract on deintercalation resulting in a loss of mutual contact. Some particles may become isolated from the rest of the electrode and hence unable to act as host for lithium insertion on subsequent discharge. The LiMn$_2$O$_4$ compounds used in early studies were prepared by the solid-state reaction between lithium carbonate and Mn$_2$O$_3$ at 850 °C in air. Alternative synthesis routes to the spinel have been reported which possess the common factor that they employ low firing temperatures and this significantly improves the capacity retention on cycling.[41–43] Our solution-based synthesis may be carried out in air and involves the reaction between Li$_2$CO$_3$ and Mn(MeCO$_2$)$_2$ in aqueous solution followed by firing at the exceptionally low temperature of 200 °C.[40,42,43] This route gives a marked improvement in the cycling performance compared with the original spinel materials. X-Ray data have shown a significant reduction in the amount of cubic (unintercalated) LiMn$_2$O$_4$ phase present at the end of discharge on extended cycling.[39] We have also found that by adding $< 1$ mass% of carbon black to the aqueous solution before firing, a dramatic improvement in the capacity retention of up to 50% after 300 cycles and at high cycling rates (currents of 1 mA cm$^{-2}$ of the electrode area), can be obtained.[42,43] Powder X-ray diffraction has demonstrated that there is a further marked drop in the accumulation of cubic material at the end of discharge when synthesised with carbon.[40] The low-temperature routes yield material of lower crystallinity as is evident from the broad peaks in the powder X-ray diffraction patterns but the particle size remains in the micron range. It may be that there is an extensive mosaic structure of small coherent crystalline regions within each particle that is better able to accommodate the volume change. Alternatively the carbon black may act as a flexible electronic contact between particles facilitating the cubic to tetragonal conversion. As well as improving capacity retention on cycling, the low-temperature synthesis yields material which depart from the stoichiometric LiMn$_2$O$_4$ composition, for example our low-temperature solution route yields, after firing at 200 °C, a composition LiMn$_2$O$_{4.1}$. These compounds are in fact cation deficient with two possible extreme cation distributions, Li$_{0.98}$[Mn$_{1.95}$□$_{0.05}$]$_{\text{oct}}$O$_4$ (where □ represents a vacant cation site) or Li$_{0.93}$[Mn$_{1.95}$Li$_{0.05}$]$_{\text{oct}}$O$_4$. LiMn$_2$O$_{4.1}$ contains 60% Mn$^{4+}$ and this implies an increase in the theoretical capacity to accept lithium from 148 to 178 mA h g$^{-1}$, *i.e.* 20% more than the stoichiometric spinel. To accommodate this, lithium ions must simultaneously occupy face-sharing octahedral (16c) and tetrahedral (8a) sites. The fact that improved overall capacity, in addition to the improved capacity retention on cycling, can be obtained from these low-temperature materials transformed the lithium manganese oxide spinels from materials with little practical interest, despite their other attributes, to compounds that are competitive for applications, Fig. 7.

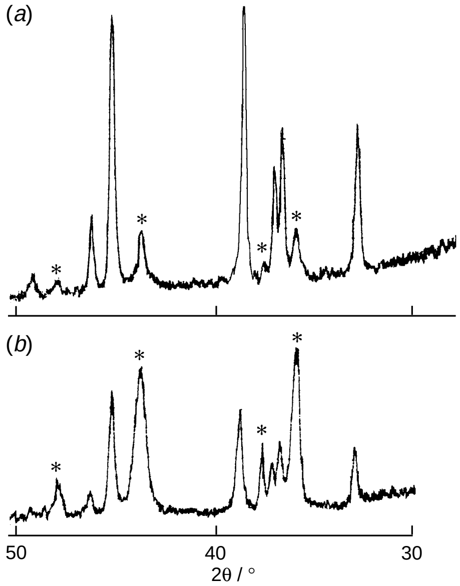

**Fig. 6** Powder X-ray diffraction patterns of electrodes constructed from LiMn$_2$O$_4$ prepared by solid-state reaction at 850 °C, (*a*) at the end of discharge after two cycles, (*b*) at the end of discharge after 50 cycles. In both cases peaks from residual cubic phase (denoted by *) are present and this phase accumulates with cycling. Cells were cycled at 0.5 mA cm$^{-2}$ between 3.7 and 2.0 V *vs.* Li$^+$/Li.

Turning now to the performance of the spinel in the 4 V regime within which lithium is extracted from the 8a sites, this appears to occur over a continuous range of solid solutions for $0.5 < x < 1$.[35,44] At *x ca.* 0.5 it has been suggested that lithium ion ordering occurs involving occupancy of one half of the tetrahedral 8a sites and that deintercalation below this composition is an event in which two cubic spinel phases of approximate composition $x = 0$ and 0.5 coexist (note that the precise composition range over which the two phases are observed is still controversial). A small step of around 100 mV between two essentially flat voltage profiles is observed at *x ca.* 0.5. Again, the original materials prepared by high-temperature solid-state reaction at 850 °C gave disappointing cycling performance, although significantly better than that in the 3 V region. Several reasons have been advanced for this.

(*i*) The two-phase nature of the process in the range $0 < x < 0.5$ leading to a cell volume change and loss of particle contact.[45] (*ii*) Dissolution of Mn$^{2+}$ in the electrolyte as a result of the disproportionation reaction $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$.[46,47] (*iii*) Electrolyte decomposition at a high degree of deintercalation *i.e.* high voltage.[48]

Probably all these factors play a role in the capacity fade of the spinel material. It has however been shown that by careful control of the composition a dramatic improvement in the

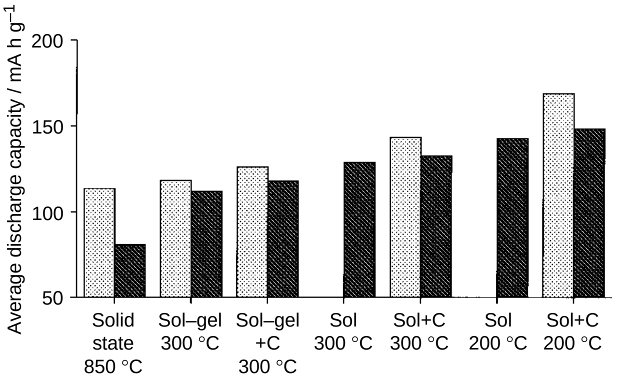

**Fig. 7** Histogram plot comparing the performance of several 3 V electrodes containing lithium manganese oxide spinels prepared under different conditions. The electrodes and cycling conditions are identical in all cases, the only difference being the active material. The discharge capacities on the *y*-axis are an average taken over the first four cycles. The cycling current densities are 0.5 mA cm$^{-2}$ (left) and 1 mA cm$^{-2}$ (right). The temperatures used to fire the spinels are shown. C refers to the addition of 1 mass% carbon black during the synthesis, 'sol–gel' refers to the use of the synthesis method described in ref. 41 and 'sol' indicates use of our own synthesis described in the text. The material prepared from the solid-state reaction was obtained by firing $Li_2CO_3$ and $Mn_2O_3$ in air.

cycling performance may be achieved.[46,49,50] Excellent cyclability can be obtained by replacing a small amount of the manganese on the 16d octahedral sites by lithium, $Li_{1+\delta}Mn_{2-\delta}O_4$ ($\delta$ = 0.1).[30,47,51] Other divalent ions *e.g.* Zn, Mg, *etc.* have also been used,[47] however lithium is attractive since it introduces no new cations into the system and a small amount of this monovalent ion corresponds to a significant increase in the average manganese valence above $Mn^{3.5+}$. This seems to be the key factor responsible for improved capacity retention on cycling. It should be noted however that such solid solutions will reduce the capacity associated with the 4 V plateau, since there is less $Mn^{3+}$ available for oxidation. It has also been shown that such solid solutions reduce dissolution of Mn and promote a single phase composition over the range $0 < x < 1$.[45] The synthesis of a spinel modified to yield an oxidation state slightly greater than $Mn^{3.5+}$ may be easily carried out by firing an aqueous mixture of $Li_2CO_3$ and $Mn(MeCO_2)_2$, first at 200 °C (*i.e.* the same conditions used to prepare a spinel for use at 3 V) and then heating at 650 °C, thus forming the non-stoichiometric spinel $LiMn_2O_{4.02}$ which is marginally cation deficient.[43,52,53] Our compound shows excellent capacity retention on cycling even at high current rates, Fig. 8. Many other solid solutions have been formed based on replacing Mn by, for example, Co, Ni, Cu, Be, Ga, Cr, *etc.*[54,55] and some of these also demonstrate improved performance. It is evident that the performance of the spinels, in contrast to $LiCoO_2$, is very sensitive to the preparative conditions.

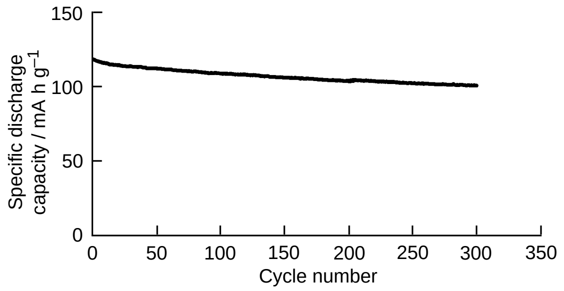

**Fig. 8** Capacity to store charge in the spinel at 4 V *vs.* number of charge–discharge cycles. Cycling was carried out between 4.3 and 3.6 V at 30 °C and at charge and discharge currents of 0.5 mA cm$^{-2}$. The electrolyte was a 1 molar solution of $LiPF_6$ dissolved in a 1 : 1 mixture of dimethyl carbonate and ethylene carbonate.

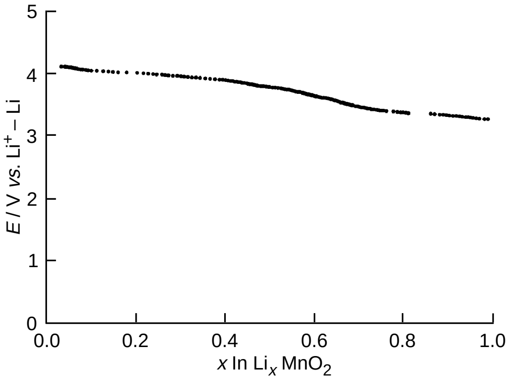

**Fig. 9** Variation of the voltage with lithium content in layered $Li_xMnO_2$ on charging at a low current (10 μA cm$^{-2}$)

## Future prospects

### *Layered $LiMnO_2$*[40,56]

Despite strenuous effects by a number of groups over the past few years the synthesis of $LiMnO_2$ with the $LiCoO_2$ structure had proved elusive until recently. Layered $LiMnO_2$ is potentially attractive since it combines the proven performance of the $LiCoO_2$ structure with the low cost and low toxicity of manganese. Furthermore, $MnO_2$ is more stable than $CoO_2$ in liquid solvents offering the possibility of obtaining the full capacity to deliver lithium compared with only half a lithium in the case of $LiCoO_2$. The difficulty is that Li–Mn–O compositions do not readily form layered structures. Very recently we have succeeded in synthesising layered $LiMnO_2$ with the structure of $LiCoO_2$ using an ion-exchange route.[40,56] Neutron powder diffraction has confirmed the layered structure. All of the lithium may be removed chemically or electrochemically yielding a total capacity of 270 mA h g$^{-1}$, Fig. 9.[40,56] Despite the high capacity, the cycling performance of these early materials is not satisfactory.[56,57] It is important to recall that the early $LiMn_2O_4$ spinels, although attractive in many ways, did not demonstrate sufficient capacity retention on cycling, however minor modification of their composition has resulted in their commercial success. The importance of layered $LiMnO_2$ may be that it opens a new avenue of exploration that will lead to optimised materials.

### *Iron Oxides*

An interesting recent development is the use of iron(III) sulfates as hosts for lithium intercalation.[58] Up to two lithiums may be reversibly inserted into $Fe_2(SO_4)_3$ accompanied by the reduction of $Fe^{3+}$ to $Fe^{2+}$. The host consists of $FeO_6$ octahedra linked by corner-sharing through $SO_4$ tetrahedra. Lithium intercalation is associated with a potential of 3.6 V *vs.* $Li^+/Li$ which is much higher than the potential associated with the same $Fe^{3+/2+}$ couple in a simple oxide. Replacement of $O^{2-}$ by $SO_4$ groups polarises the oxygens reducing the covalency of the Fe–O interactions and lowering the energy of the antibonding d levels. As a result the voltage is higher. The fact that more modest oxidation states of the first-row transition-metal ions can achieve higher voltages in these more complex framework compounds is something which deserves further exploration and may lead to a range of possibilities for the synthesis of new intercalation hosts as positive electrodes in rechargeable lithium batteries in the future.

There can be no doubt that significant advances in the performance of rechargeable lithium batteries will be achieved over the next 10 years. As was the case with the success of the first-generation systems, future development will rely heavily on the ability of solid-state chemists to rise to the challenge of designing new intercalation compounds for lithium which optimise the many different properties that are important for a positive electrode in a rechargeable lithium battery.

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## Footnotes

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† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: http://chemistry.rsc.org/rsc/cccenha.htm

‡ It should be recalled that this separation does not imply independence of these terms since ion–electron interactions must be present, only $\mu_{\mathrm{Li}}^{\mathrm{int}}$ has a rigorous thermodynamic meaning.

§ Strictly $E_F$ equates to the electrochemical potential of the electron which can include a, usually small, contribution from electric fields due to dipoles on the surface of the solid, even for an otherwise uncharged solid.[16] We shall neglect this perturbation.

¶ Note that the ion–electron interactions (including those between the $\mathrm{Li}^+$ ions and the electrons) together with the electron–electron interactions and the one-electron energy of the $e^-$ all contribute to the Fermi energy of the electron.

‖ A derivation which demonstrates that the cell voltage depends on the Fermi level difference between the two electrodes but only when they are in the cell, can be found in the enhanced version of this article on the WWW.

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