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Rechargeable Lithium Batteries [and Discussion]

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Rechargeable lithium batteries

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Much of materials electrochemistry represents a fusion of solid-state chemistry and electrochemistry. The commercial success of the world's first rechargeable lithium battery, introduced recently by Sony, is a triumph of materials electrochemistry. By developing radically new anodes, cathodes and electrolytes, a cell has been produced which can store three times the energy per unit weight and volume compared with conventional systems. This represents a revolution in battery technology. The Sony cell was developed in response to a demand from consumer electronic products such as camcorders. The future development of such products, e.g. mobile telephones and lap-top computers, of biomedical devices, such as the artificial heart, and of electric vehicles, is crucially dependent on developing advanced batteries. The markets for many of these devices are vast. The Sony cell is based on the rocking-chair concept and is composed of a carbon anode, $LiCoO_2$ cathode and non-aqueous electrolyte. The advantages and disadvantages of the rocking-chair battery will be compared with those of the rechargeable lithium battery based on a lithium-metal anode. The Sony cell represents merely a first-generation lithium system. Future substantial improvements in performance will also rely on innovative materials electrochemistry. The search for new intercalation cathodes which can offer advantages compared with $LiCoO_2$ are discussed. In particular, the development of new 3 and 4 V cathodes, based on $LiMn_2O_4$ spinel materials, is presented. These materials have a number of important advantages which make them attractive as the basis for a new generation of rechargeable lithium batteries. The new synthetic routes to the spinel materials are described, as are the structures, microstructures and electrochemical performance of these materials.

1. Introduction

For over 100 years conventional rechargeable batteries such as lead–acid or nickel–cadmium have been employed in a range of applications; they have seen steady improvement and continue to represent important technologies (Linden 1984). Battery manufacture in general is one of the fastest growing industries with over 35 batteries sold per person each year in the western world! One need only think of the vast array of modern day devices in the domestic environment that are powered by batteries, both primary and rechargeable, to gain an impression of the scale of this industry.

The 1980s, in particular, saw the development of entirely new electronic devices such as mobile telephones, lap-top computers and camcorders. They each represent multi-million pound industries and they are all crucially dependent on a mobile source of electric power that must be light in weight and compact. Conventional batteries such as nickel–cadmium were not capable of meeting this challenge (figure 1).

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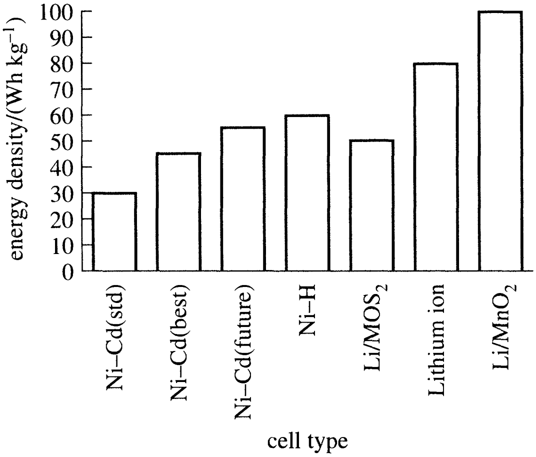

Figure 1. Comparison of different battery technologies.

Indeed the manufacturers of these electronic devices, particularly cellular telephones, acknowledged that it is no longer the electronics but the *electrochemistry* which is the *major barrier* to further development of more compact devices that also satisfy the consumer demand for additional power-hungry features. As occurred with the electronics industry in the 1940–50s a revolution in battery technology was required: then the valve was replaced by the transistor and the semiconductor revolution was born. A crucially important revolution in electrochemical technology occurred in the late 1980s with the launch of the first commercially successful rechargeable lithium battery by Sony (Nagaura 1990). This power source can store more than *three times* the energy per unit weight and volume compared with conventional lead–acid or nickel–cadmium systems, permitting the development of more compact camcorders and very recently more compact mobile telephones, which can also perform more tasks for a longer period between recharging. Other manufacturers are launching similar batteries, e.g. Toshiba, Sanyo and National Panasonic. Production has already risen to more than one million cells per month.

Batteries are by far the most important technological application of electrochemistry, whether measured in terms of numbers of cells produced, size of the industry or impact on our lives. Whereas the battery technology of the 19th century was discovered largely by serendipity, the rechargeable lithium battery is a triumph of scientific research. The commercial success of the Sony cell is an elegant demonstration of what can be achieved by combining fundamental research in solid-state chemistry and electrochemistry and then applying these together in order to achieve a technological goal. This is truly an expression of the fact that many advances can accrue from a partnership between these two scientific disciplines. Their combination is of course the focus for this Royal Society Discussion, i.e. *materials electrochemistry*.

The Sony cell represents just the first commercial step in a new electrochemical technology. The next five to ten years will see further substantial improvements in rechargeable lithium batteries. The lead–acid battery of today is far removed in its performance from that of Planté's first design!

There is, however, an even greater challenge facing rechargeable lithium battery technology than consumer electronics and that is the development of a power source for electric vehicles. This goal was the impetus for research into lithium batteries in the 1970s following the war between Israel and Egypt and the ensuing oil crisis. It is

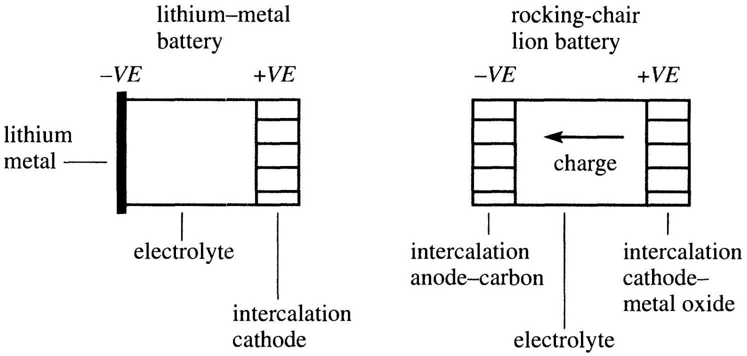

Figure 2. Schematic representation of the two main lithium battery configurations.

the hardest goal to achieve and though politically apposite in the 1970s it was not a sensible scientific or technological goal at that time. Instead the correct strategy was to develop new batteries for low-power (consumer electronic) applications, which has now been done, and only then to embark on further improving the performance of these devices towards the goal of electric vehicles. The latter will surely represent a major achievement for materials electrochemistry in the 21st century.

In this paper I shall describe the two main types of rechargeable lithium battery, discuss their relative merits and indicate how the partnership of solid-state chemistry and electrochemistry has led to new electrodes for these devices. Particular emphasis will be placed on the discovery and recent optimization of lithium manganese oxides, based on the spinel structure, as positive electrodes for future generations of rechargeable lithium batteries.

2. Rechargeable lithium battery design

Such cells divide into two basic designs (figure 2). The first and oldest consists of a negative electrode fashioned from lithium metal, a metal oxide intercalation compound as the positive electrode and a non-aqueous liquid or solid polymer electrolyte. A recent design replaces the lithium metal by a second intercalation electrode, based on carbon, and is known variously as a lithium-ion (lion), rocking-chair or a swing battery. The lithium-ion battery is fabricated in the discharged state with the lithium located in the positive electrode. On initial charging, lithium ions diffuse along channels in the intercalation host, pass into the electrolyte (liquid or solid polymer) and are transported to the negative electrode where they are inserted into the channels in the carbon host. The charge compensating electrons pass around the external circuit. Discharge reverses this process. As a result, cycling of the cell only involves the exchange of lithium ions between two, otherwise inert, hosts. The potential difference is determined by the difference in the electronic Fermi levels between the two intercalation hosts. In contrast, discharge and charging of the lithium-metal cell involves stripping and plating lithium metal at the negative electrode.

The inherent characteristics of the two cell designs are compared in table 1. The most important of these is the absence of lithium metal in the rocking-chair battery. The deposition of lithium on charging the lithium-metal cell results in a very reactive surface, often with dendrites which can lead to internal short circuits. As a consequence the rocking-chair cell is, in principle, a safer design since lithium is inserted not plated. Because it is fabricated in the discharged state, the rocking-chair

Table 1. *Comparison of lithium-metal and lithium-ion batteries*

lithium-metal battery	lithium-ion battery
potential safety problems	excellent safety—no lithium metal
plating/stripping lithium metal limits cycle-life	high cycling efficiency
very high gravimetric energy density	modest–high gravimetric energy density
very high volumetric energy density	high volumetric energy density
high cell potential	modest–high cell potential
very low self-discharge	modest self-discharge
no memory effect	no memory effect

battery may be transported to the point of sale in the safest possible condition and without the need for special precautions, unlike lithium-metal cells. The absence of lithium metal also ensures high reversibility, and hence high cycle-life, at the negative electrode. Since lithium metal cannot be stripped and plated with an efficiency in excess of 99%, a three- to six-fold excess of lithium is required even to achieve several hundred cycles from a lithium-metal battery. These features have made the lithium-ion cell the design of choice for Sony and others when developing batteries for today's consumer electronics market and it will remain so for such applications in the future. However, there are some clouds on the lithium-ion horizon, particularly in the context of developing lithium batteries for the electric vehicle market; this application demands a very high gravimetric energy density. The carbon anode used in the Sony cell has a significantly lower gravimetric and volumetric energy density than lithium metal (the maximum lithium content is $Li_{0.5}C_6$, Dahn *et al.* 1994). Higher capacity carbons are available but those with a very high capacity exhibit potential safety problems. It appears that in such materials significant quantities of lithium exist on internal surfaces, which together represent a very high surface area. Lithium on high surface area carbon must raise legitimate safety questions concerning these materials. Furthermore, the voltage of the lithium-ion cell will always be lower than an equivalent lithium-metal cell due to the more positive redox potential of carbon when compared with lithium. The lower voltage again leads to a reduction in the energy stored per unit weight and volume. If the cyclability of lithium could be improved so that the requirement for a large excess of lithium on the anode can be removed and provided a safe design can be engineered, then lithium metal may still offer the best route to a battery for the electric vehicle market. Certainly, specific military applications which take advantage of the ultimate performance of lithium-metal cells are likely.

Summarizing the current view of rechargeable lithium battery design, it is likely that the lithium-ion approach will be the design of choice for consumer electronics. Substantial improvements in the performance of lithium-ion cells are anticipated which will provide systems meeting the needs of consumer electronics into the next century. On the other hand, for very high capacities, particularly high gravimetric energy densities, lithium metal may prove the best choice, particularly if combined with suitable polymer electrolytes which have the potential to improve the safety of these systems. In short, much work, particularly in materials electrochemistry, remains to be done to build on the commercial success of the first-generation lithium-ion cell.

3. The search for positive electrodes

Having discussed the basic designs for rechargeable lithium cells and their relative merits, I shall now concentrate on the discovery and performance of intercalation compounds which are suitable as positive electrodes for such cells. This is an absolutely key issue in producing commercially viable rechargeable lithium batteries and the much needed improvements in such battery technology in the future will be critically dependent on developing new and better intercalation materials. This is not surprising when one considers that approximately 40% of the weight of a cell is associated with the cathode! Given the current importance of lithium-ion technology and the potential for lithium-metal cells I will discuss positive electrodes for both.

(*a*) *Requirements*

Table 2 presents the main requirements which an intercalation compound must satisfy if it is to be suitable as a positive electrode for rechargeable lithium batteries. First, in order to sustain high discharge and charge currents in the cell it is necessary to choose an intercalation host into which lithium may be rapidly inserted (on discharging) and from which it may be rapidly removed (on charging), i.e. a high lithium diffusion coefficient is required within the electrode material. We also wish this process to be highly reversible ensuring that the cell can be cycled many hundreds of times. Only a suitable intercalation reaction can hope to satisfy these requirements. Since the cell voltage is controlled by the difference in the Fermi level between the anode and cathode and since lithium and carbon have high Fermi levels, a large cell voltage demands the lowest possible Fermi level in the positive electrode. This in turn limits attention to intercalation compounds based on transition metal oxides (figure 3), since the oxide valence band is low enough to permit access to high oxidation state transition metal ions with, as a consequence, a low-lying Fermi level in the narrow d band formed by overlap between the transition metal d and the oxygen 2p orbitals. The Fermi levels in sulphides and selenides are typically 1–2 eV higher than in oxides. In general, intercalation of lithium into a transition metal oxide involves insertion of Li^+ ions into sites in the structure with the accompanying charge compensating electrons filling empty d-levels, thus raising the Fermi level. This leads, in turn, to a continuous decline in the cell potential upon intercalation and the characteristic 'sloping voltage profile' of such cells. In general, it is desirable to minimize this effect; we shall see later how one particularly attractive positive electrode material, $LiMn_2O_4$ can achieve this. In fact, this simple view is only partially correct, the change in chemical potential of lithium in the intercalation host (which is directly responsible for determining the change in electrode potential) arises from a change in both the chemical potential of Li^+ ions and electrons ($Li \rightleftharpoons Li^+ + e^-$). In many cases, the former dominates and it is the change in the energy of mutual repulsion between Li^+ ions which is mainly responsible for the change in electrode potential with lithium content. The intercalation electrode must also exhibit a high gravimetric and volumetric energy density. This requires first, the ability to accommodate large quantities of lithium per formula unit of the host, second a low formula weight and third a low molar volume, the last two addressing the gravimetric and volumetric energy density, respectively. The choice of an oxide was imposed above by the need to access a low Fermi level but it is also a key choice in order to ensure a minimum formula weight and hence a high gravimetric energy density compared with sulphides or selenides. For the same reason our choice of oxide will be limited to the first row transition metal ions, these will also provide us with the lowest possible

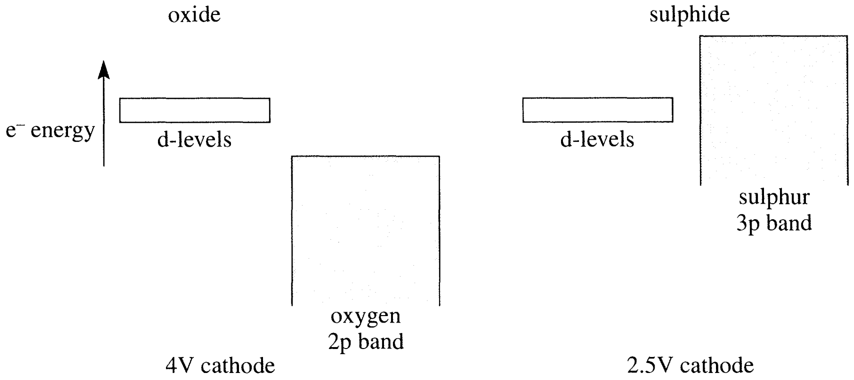

Figure 3. Electronic energy level diagram for a binary transition metal oxide and sulphide with the same transition metal ion in the same oxidation state, in each case.

Fermi level since the 3d levels are, in general, below those of 4d and 5d. Some classes of intercalation host permit intercalation of the solvent molecules from the electrolyte along with the lithium ions. This is generally undesirable leading to a breakup of the structure and consequently inferior cycle-life; intercalation hosts should be chosen to avoid this. Crucial to obtaining a long shelf-life, high cycle-life and low self-discharge on open circuit, is the stability of the electrode in contact with the electrolyte. Suitable electrolytes have to exhibit stability to reduction at the negative and oxidation at the positive electrode, this requires a salt and solvent which are stable within the range 0 to 4 or 4.5 V versus Li^+(1 M)/Li. In particular, the possibility of catalytic decomposition on the transition metal oxide surface is an important consideration. Finally, but arguably of greatest significance when developing a consumer product for the 21st century, are the twin needs of a material which is environmentally acceptable and cheap. The latter is particularly important for battery electrodes since each cell would contain several grams of material and the numbers of such cells that are envisaged run to tens of millions per year. This is in contrast to electrochemical materials such as surface modifying electrocatalysts which may be very expensive per gram but are used in such small quantities that their high cost can be more easily tolerated.

It is evident from table 2 and the previous discussion that the extent and diversity of properties which must be combined in one intercalation host, if it is to be a successful positive electrode in a rechargeable lithium battery, makes identification of such a compound a formidable task. Table 2 alone serves as a testimony to the adage that it is easier to carry out fundamental research than it is to develop materials that will perform well in a technological application!

(*b*) *Positive electrodes—the candidates*

Considering first cathodes for the lithium-ion cells since these have received the greatest attention recently, three candidates have emerged, $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$. The first two are isostructural layered compounds consisting of cubic close-packed oxide ions with the sheets of octahedral sites between adjacent oxide layers being occupied alternately by Li^+ and Co^{3+} or Ni^{3+}, respectively. $LiCoO_2$ is an essential component in the success of the first-generation lithium-ion cell marketed by Sony. Its potential as a positive electrode for rechargeable lithium batteries was first recognized and investigated in Oxford in the early 1980s (Thomas *et al.* 1985*a*,

Table 2. *Requirements for a positive electrode material*

1	must be an intercalation host for lithium
2	sustain high rates of lithium intercalation and deintercalation → high cell discharge–charge rates
3	highly reversible lithium intercalation → many charge/discharge cycles
4	low Fermi level → high open circuit voltage
5	potential invariant with lithium content → cell potential invariant with state of charge
6	capable of accommodating large quantities of lithium per formula unit → high capacity
7	low formula weight → high gravimetric energy density
8	low molar volume → high volumetric energy density
9	avoid co-intercalation of solvent
10	stable in contact with candidate electrolytes
11	adequate electronic conductivity
12	low cost
13	easily fabricated into composite cathode
14	environmentally friendly

b, Mizushima *et al.* 1980). Although at the time of Sony's development work on the lithium-ion cell, $LiCoO_2$ was the electrode which exhibited the best performance, it does have a number of drawbacks which contribute significantly to limiting the performance of the first-generation lithium-ion batteries. These are, its high cost (cobalt is twice the price of nickel and ten times that of manganese), limited range of lithium content over which it is stable on cycling (approximately between $Li_{0.45}CoO_2$ and $LiCoO_2$), the possibility of cointercalation of solvent between the layers and the toxicity of cobalt compounds. $LiNiO_2$ exhibits a higher capacity for lithium cycling but some reports suggest that the nickel ions disorder in the lithium layers (Delmas 1994). Solid solutions such as Li $(Ni_{1-x}Co_x)O_2$, can offer a compromise between stability, cost and capacity and are being pursued in some quarters (Delmas 1994). The third compound in our list, $LiMn_2O_4$, is widely regarded as an attractive option. It fulfils to a high degree the requirements listed in table 2. In particular, its cost per gram is very much less than its rivals and it is regarded as environmentally more benign than the others. In addition, manganese oxides, albeit with different crystal structures, are already very familiar to the battery industry who are thus used to handling and processing them. These advantages make $LiMn_2O_4$ attractive for use in future cells which are targeted on consumer electronic products where high-volume production is envisaged. The manganese oxides are also regarded as particularly attractive for electric vehicle applications where large quantities and low material costs per mile are crucial criteria. Following the early work on $LiMn_2O_4$, extensive studies have taken place aimed at the preparation of new Li–Mn–O phases, e.g. $Li_2Mn_4O_9$ (Thackeray *et al.* 1992).

$LiMn_2O_4$ adopts the spinel structure (cubic space group $Fd\bar{3}m$) consisting of cubic close-packed oxide ions with the manganese ions in one-half of the octahedral sites (designated 16(d) in the Wyckoff notation) and Li^+ ions in one-eighth of the tetrahedral sites (designated 8(a)). It is a remarkable material since it can operate as both a 3 and 4 V cathode in lithium cells (voltages quoted versus the Li^+ (1 M)/Li couple). Its fundamental properties as an intercalation host for lithium were first discovered and investigated in the UK during the early 1980s (Thackeray *et al.* 1983, 1984; Goodenough *et al.* 1984). Virtually all the lithium can be removed from $LiMn_2O_4$ with the corresponding oxidation of Mn^{3+} to Mn^{4+}, thus yielding an otherwise unattainable polymorph of manganese dioxide, $MnO_{2-\lambda}$. This process is associated with a flat voltage profile of 4 V versus Li^+ (1 M)/Li. The origin of the flat voltage is not yet well understood in this case. It, however, signals that $LiMn_2O_4$ does not undergo lithium deintercalation by passing through a continuous range of solid solutions, but instead a two-phase process occurs with each phase exhibiting a constant composition and hence lithium chemical potential, ensuring a constant electrode potential on charge and discharge. A similar flat voltage response is observed on insertion of lithium into $LiMn_2O_4$ but this time the voltage is 3 V versus Li^+ (1 M)/Li. A maximum composition slightly in excess of $Li_2Mn_2O_4$ may be obtained. The origin of the flat voltage response is now well understood in this case (Thackeray *et al.* 1983; Goodenough *et al.* 1984). Half the manganese in $LiMn_2O_4$ is Mn^{3+} and half Mn^{4+}. The former is a Jahn–Teller active ion ($3d^4$) and would be stabilized by distortion of its octahedral oxygen environment to a lower symmetry. However, this would consume elastic strain energy and since all the Mn octahedral sites would have to distort together, but only 50% (the Mn^{3+} ions) can gain electronic stabilization, this does not occur. On intercalation of lithium, Mn^{4+} is reduced to Mn^{3+} just inside the surface of the $LiMn_2O_4$ particles, increasing the proportion of the Jahn–Teller active ions and inducing a spontaneous distortion to tetragonal symmetry at each manganese site with an associated lowering of the overall crystal symmetry from cubic to tetragonal. The near-surface region now consists of tetragonal $Li_2Mn_2O_4$, whereas the core of the particles remain as cubic $LiMn_2O_4$. On further intercalation the phase boundary between the cubic and tetragonal structures moves, consuming cubic material and converting it to the tetragonal phase. As a result a constant difference in lithium chemical potential and hence a constant voltage is obtained. The minor nature of the Jahn–Teller-induced distortion, which does not require diffusion of framework manganese or oxide ions, appears therefore to be facile, hence rapid insertion and removal of lithium is possible. The process of intercalation and deintercalation associated with the 4 V region between $MnO_{2-\lambda}$ and $LiMn_2O_4$ also appears to be facile.

The Mn_2O_4 framework of $LiMn_2O_4$ is shown in figure 4. Evident in this figure is the set of channels formed by empty face-sharing tetrahedral and octahedral sites which are interconnected in three dimensions thus forming pathways for the diffusion of lithium into and out of the structure. The ease of diffusion within the Mn_2O_4 host is clear from this representation.

$LiMn_2O_4$ therefore appears to satisfy many of the criteria presented in table 2. However, the early materials, though fascinating scientifically since they represented the discovery of a new class of three-dimensional intercalation hosts at a time when concentration was being placed on two-dimensional (layered) structures, were entirely unsatisfactory as cathodes in rechargeable lithium batteries. This is shown in figure 5 which presents cycling data for the early materials (Bruce 1993). Evidently, after only a few tens of cycles the capacity to store lithium in the material, and hence charge in the cell, falls dramatically and to unacceptably low levels. The $LiMn_2O_4$-based materials which today represent the basis for positive electrodes in rechargeable lithium cells are prepared quite differently from these early compounds and as a result provide excellent cycle-life while retaining the other attractive fea-

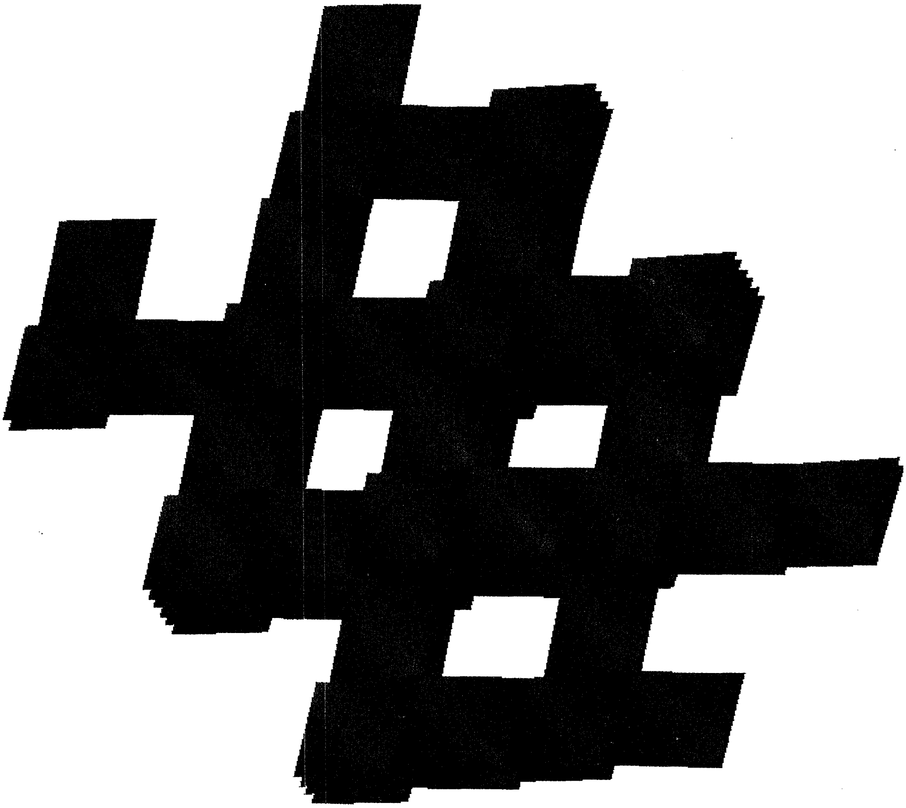

Figure 4. The Mn_2O_4 framework of $LiMn_2O_4$. Octahedra represent MnO_6 groups which share common edges.

tures of manganese oxides. The recent developments of high-performance positive electrodes are described in the next section.

4. Discovery of high-performance positive electrodes

The early $LiMn_2O_4$ materials were prepared by conventional high-temperature solid-state reactions carried out at 850 °C between Li_2CO_3 and Mn_2O_3 in air. By developing new synthetic routes including those based on sol-gel or solution methods, the necessary radical improvement in cycle-life has been achieved (Huang & Bruce 1994*a*, *b*, 1995; Pistoia & Wang 1993; Barboux *et al.* 1991; Tarascon & Guyomard 1993; Momchilov *et al.* 1993). In particular, we have designed recently a solution-based synthesis which has the advantages of being a low-cost route, involving only aqueous solutions, low temperatures and capable of being carried out in air, unlike alternative sol-gel methods. It is particularly well suited to scaling up for industrial production. Both 3 and 4 V materials have been prepared by solution routes, each optimized for performance within their respective voltage regimes. These materials satisfy all the requirements in table 2 including sustaining excellent cyclability. The 4 V materials are of interest particularly as positive electrodes in lithium-ion cells, whereas the 3 V materials are attractive in the context of a lithium-metal anode-based battery.

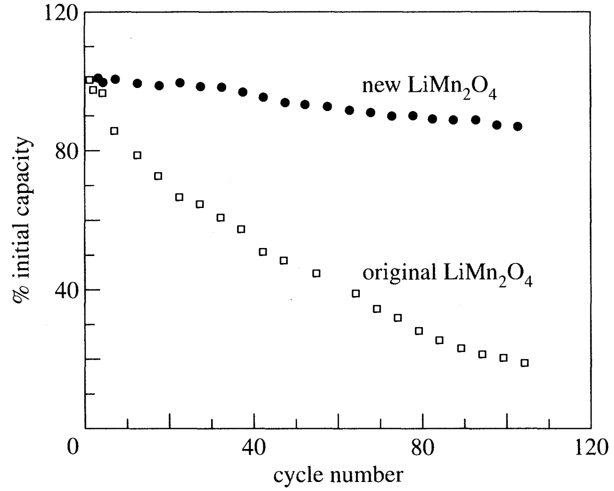

Figure 5. Cyclability of cathodes based on $LiMn_2O_4$ prepared by high-temperature solid-state reaction (□), and by a new solution route, (●). Three electrode cells were used with the manganese oxides as the working electrodes. The decline in capacity was calculated from the reduction in charge stored by the cathode on each cycle between fixed voltage limits. The very significant improvement in the ability to store charge on cycling the cell with the solution-based electrode is evident.

(*a*) 3 V *cathodes*

The materials which form the basis of the 3 V cathodes are synthesized by reaction between $Mn(CH_3COO)_2 \cdot 4H_2O$ (Aldrich 99+%) and a solution of Li_2CO_3 (BDH, 99.5%) in distilled water. Sufficient manganese (II) acetate was used to yield a 2:1 mole ratio of manganese to lithium. A small amount of carbon (less than 1% by weight of $Mn(CH_3COO)_2 \cdot 4H_2O$) was introduced into the mixture which was then subjected to vigorous stirring. A precipitate formed, the remaining water being removed first by rotary evaporation at 85 °C followed by drying in air at 200 °C for four days (Huang & Bruce 1994*a*, 1995). To study the influence of carbon on the properties of the electrodes some materials were prepared exactly as described previously but without the addition of the carbon during the synthesis. The powder X-ray diffraction pattern for the new material indicates that it does adopt a spinel structure, however, the peaks are much broader than is the case for the sample prepared by solid-state reaction at 850 °C (figure 6). This is indicative of a much smaller particle size, considerable strain or disorder in the lattice of the materials prepared in solution. Transmission electron microscopy carried out on the new materials revealed an average particle size of approximately 200–300 Å (figure 7). The composition of the material prepared by the solution route is $LiMn_2O_{4.1}$, as determined by a sequence of redox titrations involving MnO_4^-/Mn^{2+} and Fe^{3+}/Fe^{2+} couples (Huang & Bruce 1995; Vetter & Jaeger 1966). Being more highly oxidized than the stoichiometric material, $LiMn_2O_{4.1}$ has a greater theoretical capacity for lithium, 176 mA h g^{-1} compared with 148 mA h g^{-1} for $LiMn_2O_4$. The key test for cathode material performance is to subject it to constant current cycling between fixed voltage limits and to monitor its ability to store charge under these conditions. In order to do this cells were prepared in the following way. The active material was ground together with carbon black and PTFE in the weight ratios 80 : 13 : 7. The mixtures were pressed on to aluminium grids, typically with a loading of 16 mg cm^{-2}, and the entire assembly was then dried under a vacuum at 80 °C for 12 h. Three electrode cells were con-

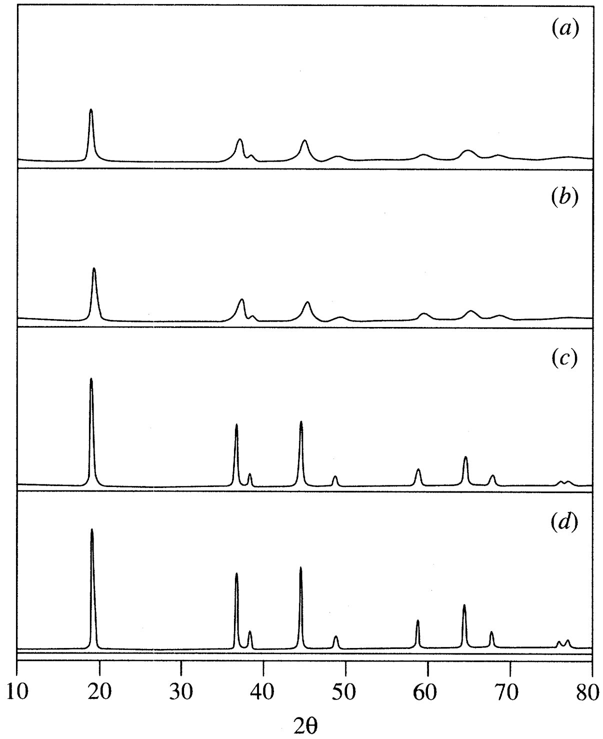

Figure 6. Powder X-ray diffraction patterns for lithium manganese oxide spinels: (*a*) $LiMn_2O_{4.1}$ synthesized from solution then fired at 200 °C; (*b*) $LiMn_2O_{4.1}$ synthesized from solution with carbon then fired at 200 °C; (*c*) $LiMn_2O_4$ synthesized from solution then fired at 600 °C; (*d*) synthesized by solid-state reaction between Li_2CO_3 and Mn_2O_3 at 850 °C.

structed from the composite cathode, a lithium-metal reference and a lithium-metal counter electrode. The electrolyte consisted of a 1 M solution of $LiAsF_6$(LITHCO) dissolved in propylene carbonate (Aldrich 99+%). The salt was used as received but the propylene carbonate (PC) was rigorously purified using a Fischer HMS 500 C distillation apparatus with 90 theoretical plates. Cycling of the composite cathodes was carried out galvanistatically between 3.7 and 2.0 V with respect to the lithium-metal reference, and at discharge and charge currents of 1 and 0.5 mA cm^{-2}, respectively (the discharge rate was $C/2$). The specific discharge capacities for each cycle are presented in figure 8; these are based on the weights of lithium manganese oxide in the composite cathodes. In the case of the lithium manganese oxide prepared with carbon (less than 1 wt%) the initial capacity is in excess of 140 mA h g^{-1} (compared with the theoretical capacity of 176 mA h g^{-1}) and rises slightly within the first few cycles, subsequently falling to 125 mA h g^{-1} at 100 cycles, 100 mA h g^{-1} at 200 cycles and 90 mA h g^{-1} at 300 cycles.

The influence of adding carbon, during the solution stage of the synthesis, on the cyclability is evident in figure 8. Although the initial capacity is similar with or without carbon, the capacity fade is significantly less if carbon is used. The capacity after 300 cycles is approximately 50% higher. Studies have shown that the optimum amount of carbon is approximately 1 wt%. We are investigating the mechanism by which carbon minimizes the capacity fade on cycling. The powder X-ray diffraction patterns of the materials with and without carbon are identical as are the composi-

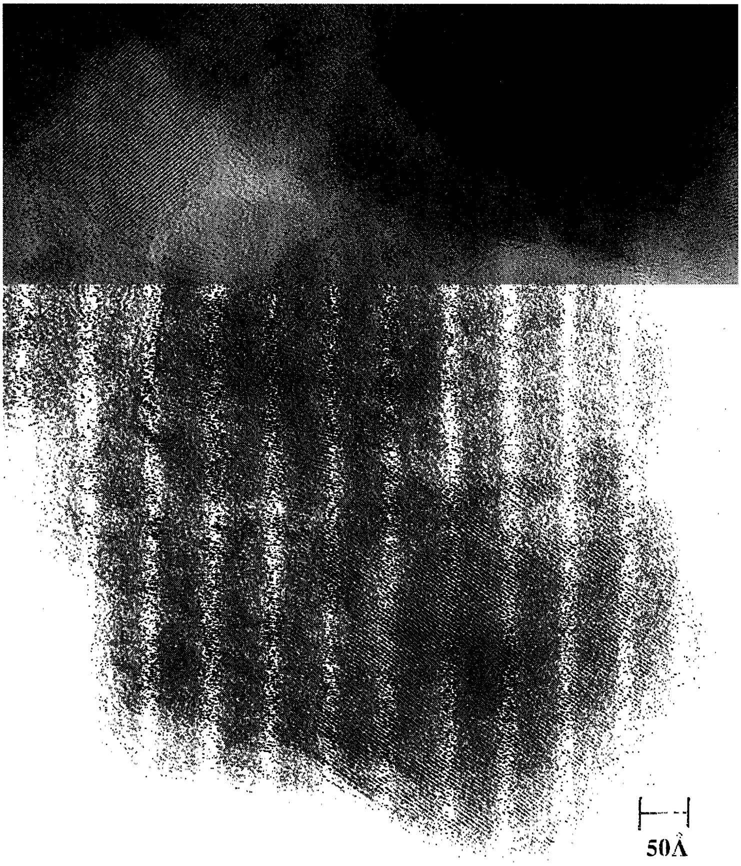

Figure 7. (*a*) Transmission electron micrographs for $LiMn_2O_{4.1}$ prepared from solution and fired at 200 °C.

tions (figure 6). Electrical measurements indicate that carbon does not enhance the interparticle electronic conductivity. By dissolving the spinel we have verified that carbon is still present in the sample after the heating cycle at 200 °C for four days. As yet we have no clear explanation for the remarkable improvement in performance with carbon. The gain is even more attractive from a commercial viewpoint when one considers the minimal cost of adding such a small amount of carbon during the solution stage of the synthesis. Studies aimed at elucidating the role of carbon are continuing.

The major improvement in performance which has been obtained in recent years by developing new synthetic routes is evident in figure 9. The histogram plot highlights the low capacity of the cathodes prepared by solid-state reaction and the sensitivity of this capacity to the current density (discharge rate). Doubling the discharge current

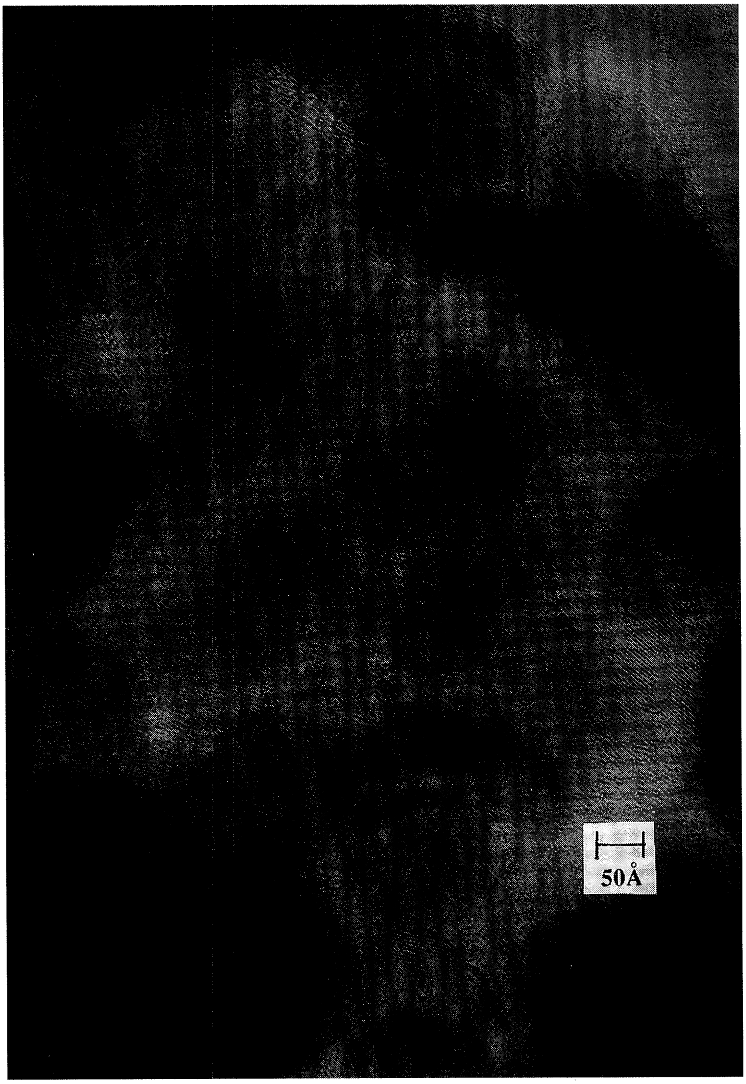

Figure 7. (*b*) Transmission electron micrographs for $LiMn_2O_4$ prepared from solution and fired at 600 °C.

density almost halves the capacity. The progress that has been achieved by moving first to a sol-gel and then to a solution route, by lowering further the temperature from 300 to 200 °C and by adding carbon, is clearly illustrated in figure 9. We have found that the best performance may be obtained by using our solution synthesis including carbon and firing the precipitate at 200 °C. The discharge capacity at the highest rate of $C/2$ has been doubled in changing from a solid-state reaction at high temperature to our low-temperature solution route! Although we do not as yet understand fully the origin of enhancement due to carbon, it is evident that the particularly low firing temperature of 200 °C that becomes possible with the solution route, yields small particles which, in turn, assures a high surface area in contact with the liquid electrolyte in the cells. This results in a lower concentration polarization at high current densities than would otherwise be obtained.

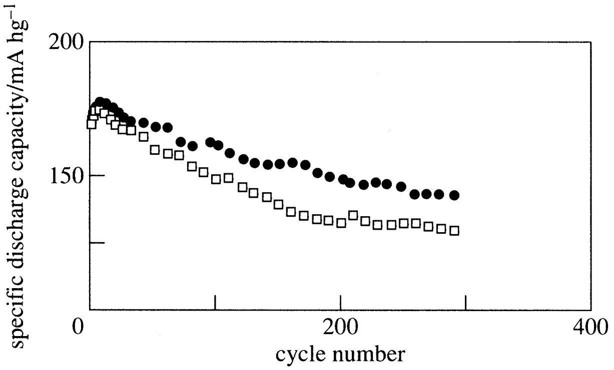

Figure 8. Variation of specific discharge capacity with the number of cycles for the 3 V composite cathodes containing, $LiMn_2O_{4.1}$ synthesized from solution at 200 °C with carbon (●) and without carbon (☐). Cycling was carried out galvanostatically at discharge and charge current densities of 1 mA cm^{-2} and 0.5 mA cm^{-2}, respectively, and between 3.7 and 2.0 V. The discharge rate was $C/2$.

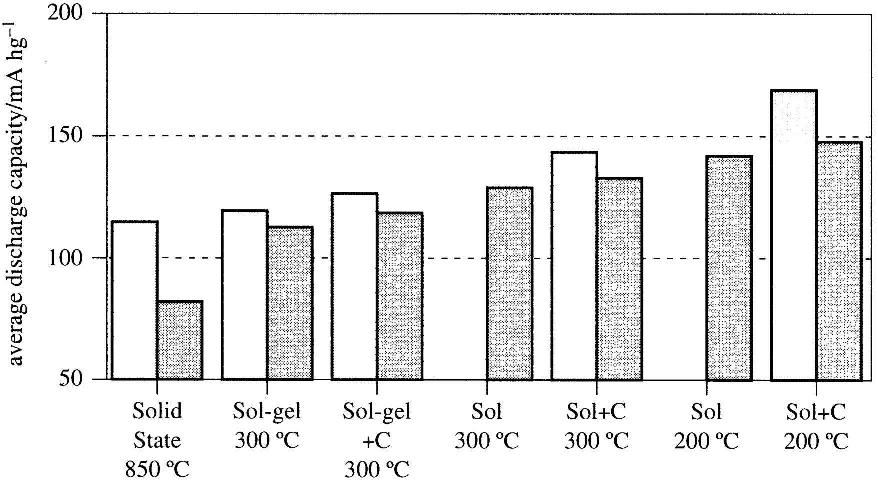

Figure 9. Histogram plot comparing the cycling performance of several 3 V composite cathodes containing lithium manganese oxide spinels prepared under different conditions. The composite cathodes and cycling conditions were identical in all cases, the only difference being the active material. The specific capacities are an average taken over the first four cycles. The charging rate is $C/4$ and the discharge rates are $C/4$ for the light-grey shaded bars and $C/2$ for the dark-grey shaded bars.

(*b*) 4 V *cathodes*

The active materials are synthesized using a similar solution route to that of the 3 V materials, except that carbon is not added during the solution stage and after firing at 200 °C the temperature is raised to 600 °C for 8–12 h (Huang & Bruce 1994*b*, 1995). The powders are fired at 200 °C before heat treatment at 600 °C in order to lock-in a small average particle size which is generally desirable for cathode performance (figure 7). Again, powder X-ray diffraction confirms the existence of a spinel structure (figure 6). However, the peak width at half height is much less than is the case for material fired only at 200 °C, although still greater than the peak width obtained by solid-state reaction at 850 °C. Given that the particle size of both the 3 and 4 V material is small and similar, we must conclude that heating at 600 °C has

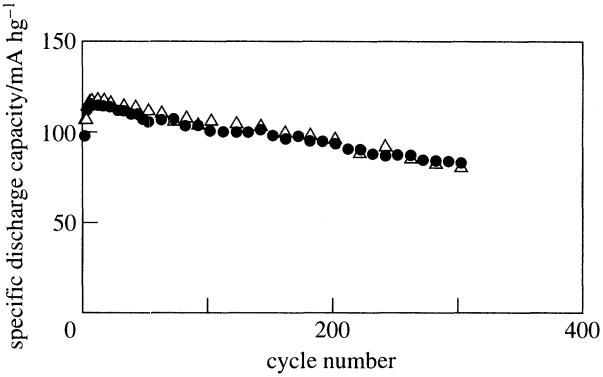

Figure 10. Variation of specific discharge capacity with the number of cycles for 4 V composite cathodes containing, $LiMn_2O_4$ synthesized from solution at 600 °C with carbon (●) and without carbon (△). Cycling was carried out galvanostatically at discharge and charge current densities of 1 mA cm^{-2} and 0.5 mA cm^{-2}, respectively, and between 4.4 and 3.3 V. The discharge rate was $C/2$.

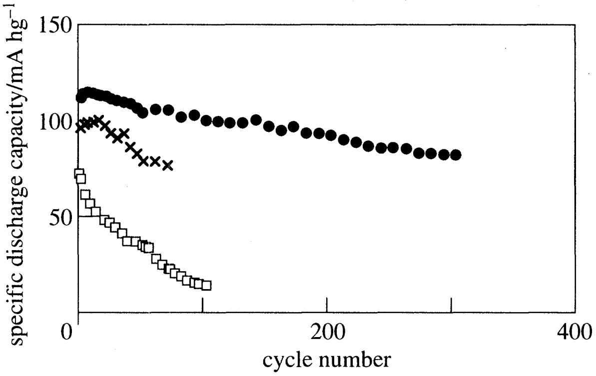

Figure 11. Variation of specific discharge capacity with the number of cycles for three composite cathodes. Cycling was carried out galvanostatically at discharge and charge current densities of 1 and 0.5 mA cm^{-2}, respectively, and between 4.4 and 3.3 V. The discharge rate was $C/2$ (●) $LiMn_2O_4$ prepared from solution and fired at 600 °C, (□) $LiMn_2O_4$ prepared by solid-state reaction, (×) $LiMn_2O_{4.1}$ synthesized from solution and fired at 200 °C.

removed significant strain or disorder in the structure. This may be related to the composition of the 4 V material which is closer to the stoichiometric spinel $LiMn_2O_4$ than is the 3 V compound.

The crucial cycling performance is shown in figure 10. The fabrication of the composite cathode and the electrochemical cell are identical to that described previously for the 3 V material, except that the electrolyte now consists of a 1 M solution of $LiClO_4$ in propylene carbonate. Cycling was carried out galvanostatically between 4.4 and 3.3 V versus Li^+(1 M/Li) and at discharge and charging current densities of 1 and 0.5 mA cm^{-2}, respectively—the discharge rate was again $C/2$. Capacities are quoted per gram of the active material. The initial discharge capacity is 110 mA h g^{-1}, rising very slightly on the second cycle and then declining by only 10 mA h g^{-1} to 100 mA h g^{-1} at 100 cycles, 90 mA h g^{-1} at 200 cycles and 85 mA h g^{-1} at 300 cycles. This represents very good capacity retention, particularly in view of the relatively high current densities and depth of discharge. Figure 10 also indicates the effect of adding carbon during the solution synthesis in the case of the 4 V material.

Evidently, no enhancement is obtained, in complete contrast to the results for the 3 V compound.

It is interesting to compare the cycling performance of our new 3 and 4 V materials (figures 8 and 10). It is evident that for electrodes prepared in an identical manner, except for the nature of the active material and cycled at the same current densities, the capacity fade is significantly greater in the case of the 3 V material. This is probably related to the fact that there is a well defined phase transition between the cubic and the tetragonal structure on each cycle. X-ray diffraction data collected by us as a function of the number of cycles indicates a certain degree of irreversibility in this transition which may well explain the greater capacity fade. It is also interesting to compare the performance of the 3 V material when cycled in the 4 V regime and vice versa. In both cases the cyclability is markedly inferior when carried out in the 'wrong' voltage range. This is illustrated by comparing figures 8 and 11. Cycling the 3 V material in the 4 V regime is expected to yield a lower capacity than when the same material is cycled in the 3 V regime. However, the 3 V material also suffers greater capacity fade when cycled in the 4 V regime. The 3 V material can only achieve a capacity of 75 mA h g^{-1} after 80 cycles, figure 11. These results reveal that despite the fact that both the 3 and 4 V materials are based on the lithium manganese oxide spinel, the materials are, in fact, quite different. In particular, the differences in composition (and hence theoretical capacity), defect structure and strain in the lattice arising from the differences in their preparation, identify each of them as highly distinctive compounds in terms of their performance in composite cathodes for rechargeable lithium batteries. This work also provides an important lesson in materials electrochemistry. It is clear that all the parameters of a solid-state material including composition, structure, defect structure and microstructure must be optimized in order to obtain the best possible performance. This point is emphasized further in figure 11 by the inclusion of data for the solid-state material fired at 850 °C.

In conclusion, the performance of the 3 and 4 V materials prepared by the solution-based routes when combined with the advantages of these routes in terms of scale-up and cost, has resulted in intensive world-wide interest in the materials. Work is already taking place in the UK and internationally involving the testing of prototype lithium-ion batteries based on these positive electrode materials. In particular, the 4 V materials are set to form the basis of a new generation of rechargeable lithium-ion batteries.

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Discussion

R. CAHN (*Department of Materials Science, Cambridge University, UK*). One is told that some batteries, those used for camcorders in particular, need to be completely discharged before recharging, lest they be permanently damaged. How do the batteries Professor Bruce has been telling us about measure up in this respect?

P. G. BRUCE. I believe Professor Cahn is referring to the phenomenon known as the ‘memory effect’, which can plague nickel–cadmium batteries. If such a fully charged cell is then partly discharged followed by recharging, subsequent discharge will only yield the amount of energy inserted on the recharge; in other words, the practical capacity of the cell has been significantly depleted! This does not permanently damage the cell but it does require forced and complete discharging of the cell in order to recover the full capacity. The memory effect is *not* present in lithium-ion cells and this is one of the significant advantages compared with nickel–cadmium systems.

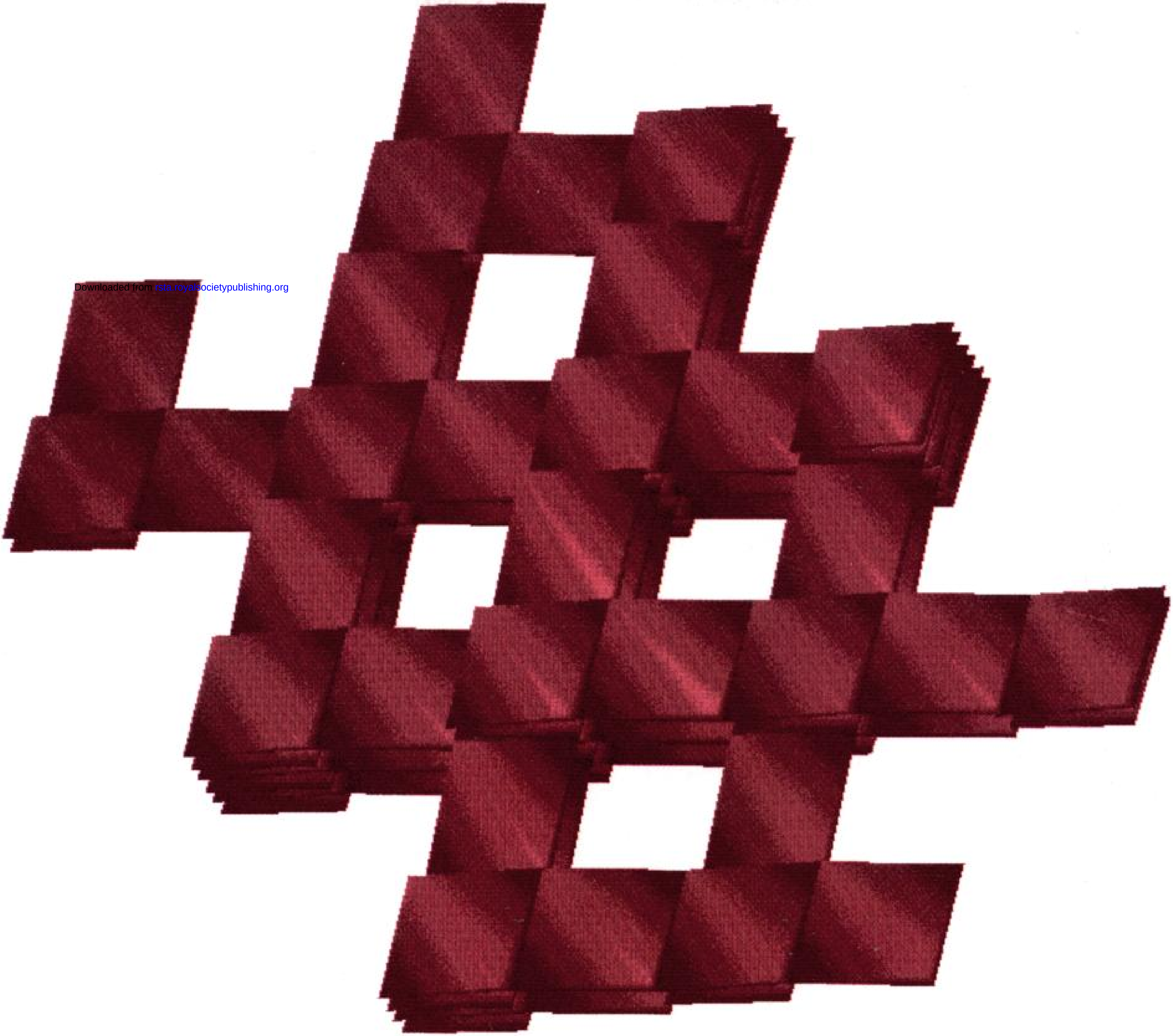
N. E. BAGSHAW (*Consultant, Stockport, UK*). Mention has been made of the use of secondary lithium batteries for electric vehicles and I believe that there is a project underway in Japan for load levelling applications. Can Professor Bruce tell us what is the biggest secondary lithium battery so far available, and how long it will be before batteries exist for commercial use in electric vehicles and load levelling?

P. G. BRUCE. Secondary lithium-ion batteries are already a commercial reality with production in excess of one million cells per month and several manufacturers now in the market place. These cells are capable of storing 100–120 Wh kg^{-1} and 280 Wh l^{-1}. This represents a two- to three-fold improvement compared with conventional nickel–cadmium or lead–acid systems. However, the cells currently available are targeted on the consumer electronics market, i.e. they are relatively low power systems. The main challenges in developing lithium-ion cells for traction are the need to use lower cost materials, improve rate capability and some improvement in cycle life. To my knowledge there is not yet a commercially available rechargeable lithium battery for electric traction. There are, however, several prototype systems which have been developed in the USA, Japan and Europe. Systems of around 20 kWh have been produced in Europe. Since several problems have, I believe, yet to be solved before commercially viable lithium-ion batteries are available for electric vehicles, I would not wish to place a timescale on this at present.

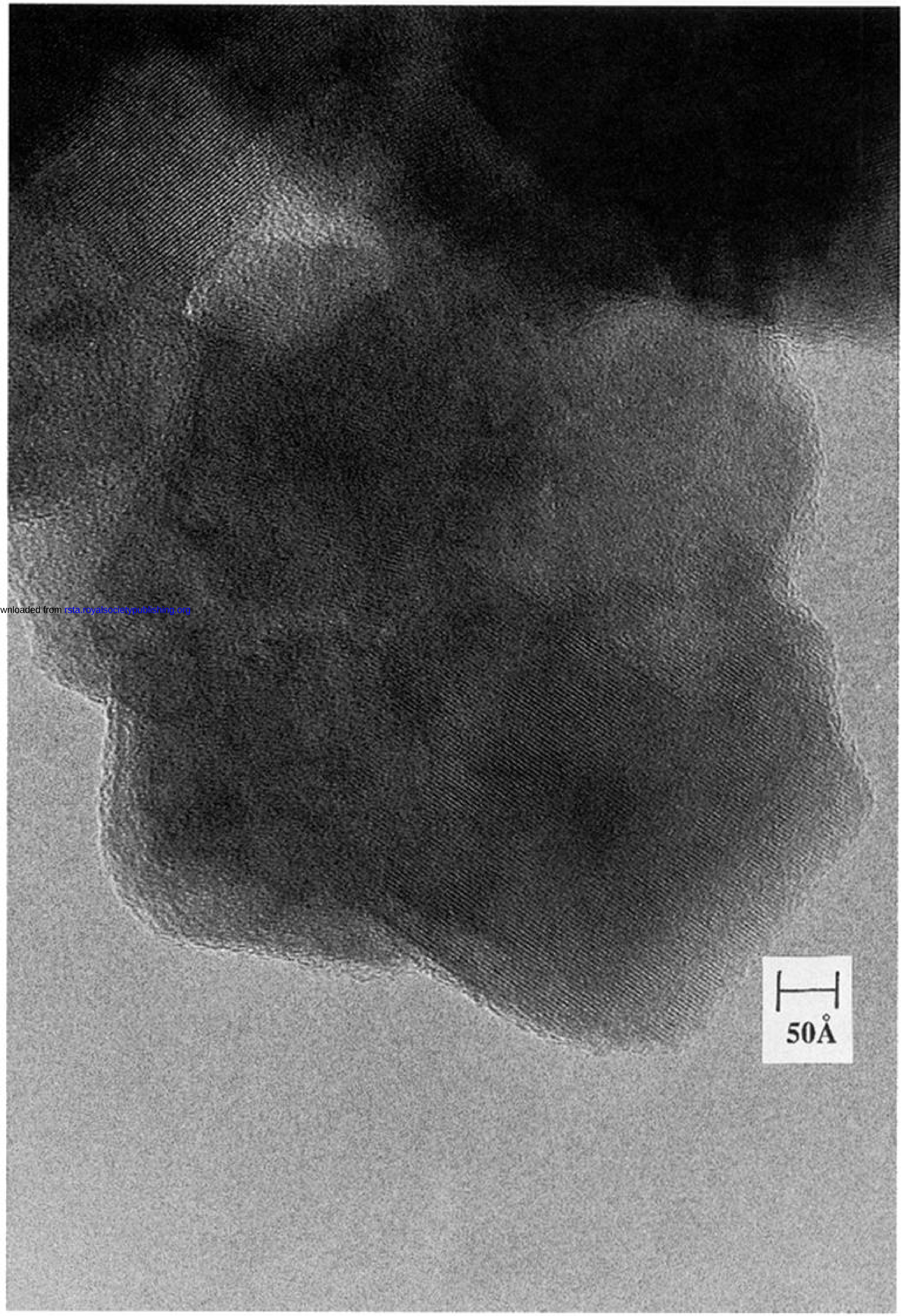
In the context of load levelling where weight and to some extent size are less pressing aspects of the design criteria, I remain to be convinced that lithium-ion systems have a great advantage to offer.

A. Hamnett (*Department of Chemistry, University of Newcastle, UK*). The requirement of a low Fermi level is being satisfied by exploitation of low-lying d-levels in first-row transition elements. However, if we look at the periodic table, there are other low-lying orbitals that could be exploited, including the s^2 orbital in the heavier B-metals. Has this type of energy level been exploited in Li battery cathodes?

P. G. Bruce. Professor Hamnett is of course correct in that low Fermi levels are available from the s orbitals of the heavy B-metals. However, the requirement for light-weight materials in combination with a low Fermi level confines our attention to transition metal oxides from the right-hand side of the first transition series, i.e. Mn, Fe, Co and Ni.



gure 4. The Mn_2O_4 framework of $LiMn_2O_4$. Octahedra represent MnO_6 groups which share common edges.



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