Rechargeable lithium batteries

(b)

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The market for lithium batteries is undergoing a rapid expansion as new applications demand higher densities of energy and power storage. Simple theoretical estimates show that lithium and lithium ion cells can reach specific energies of 880 and 500 W h kg^{-1} respectively. With an electrolyte conductivity above 3×10^{-4} S cm^{-1} and thickness below 0.01 cm, a power density of 300 W dm^{-3} can be obtained without excessive energy losses. Diffusion in porous or polymer composite electrodes is enhanced by an inter-penetrating electrolyte provided the electrode particles are small. Batteries using transition metal oxide positive electrodes and carbon negative electrodes are expected to give practical specific energies up to 180 W h kg^{-1} including packaging and other essential additional materials in the near future.
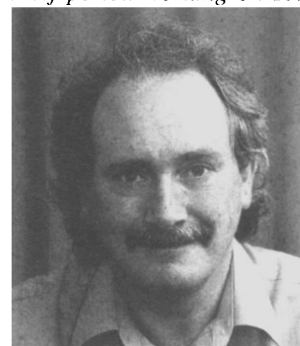
1 Introduction

1.1 Market requirements
At the time of writing there are many new electrical technologies which require rechargeable batteries, for example:

- information technology—*e.g.* camcorders, digital cameras and personal computers;
- portable machine tools—*e.g.* power drills, saws, sanders *etc.*;
- electric traction—*e.g.* various vehicles from golf carts to electric buses.

Apart from a rapidly expanding market, what these have in common is that the ultimate performance is now restricted by the power capability and energy storage capacity of the battery. The performance of the product will be determined by the specific power (W kg^{-1}) or power density (W dm^{-3}) of the battery. A high specific power is required to meet the power demand of the product, within the battery mass or volume constraint, whichever is limited. The specific energy (W h kg^{-1}) or the energy density (W h dm^{-3}) of the battery, along with the power consumption of the product, determine the period of useful use before recharge is required. In addition, a

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reasonable lifetime is expected of the battery; this is usually defined in terms of the cycle life, *i.e.* the total number of charge–discharge cycles which may be obtained before a significant degradation occurs in the energy and power values.

Specific energy, power and cyclability values of most commercial rechargeable batteries have been of secondary importance to the unit cost; for example the relatively cheap lead–acid system delivers less than 50 W h kg^{-1} and the cycle life is low for deep cycling. Furthermore, the new environmental legislation which will require recycling of heavy metals is now beginning to increase the real cost of batteries containing lead or cadmium.

Some main targets for a high energy density battery have been described as:[1]

- Specific energy—180 W h kg^{-1};
- Energy density—360 W h dm^{-3};
- Cycle life— > 500.

The situation is therefore quite different from that of batteries for automotive engine starting, where improvements in the batteries offer only a marginal benefit. In the case of portable computers, tools and electric vehicles, any improvements in the battery will translate directly into increased profit. High-energy and -power batteries are therefore a unique opportunity for investment.

1.2 New developments
As a consequence of the situation described above, a rapid expansion in research on rechargeable batteries has occurred over the last two decades. Traditional batteries such as lead–acid and nickel oxide–cadmium have benefited from physical design improvements to improve energy and power density and incorporate new features such as overcharge protection. Concurrently, some new systems have developed which are based on entirely new chemistry. Perhaps the greatest conceptual leap in the battery design was the use of non-aqueous electrolytes to allow the use of lithium or sodium metal as the negative electrode. This has two effects: first, the mass and volume of the negative electrode (*e.g.* Li) can be very small in comparison with the positive electrode (*e.g.* MnO$_2$), resulting in almost double the specific charge (A h kg^{-1}); secondly, the energy per unit charge stored (*i.e.* the potential difference) is also doubled, or almost tripled in comparison with the nickel oxide–cadmium system.

A comparison between some traditional and novel battery systems is shown in the Ragone plot of Fig. 1. It may be seen that lithium batteries occupy the prime position.

1.3 Lithium batteries
A schematic diagram of a single cell of a rechargeable lithium battery is shown in Fig. 2(*a*). Compared with some aqueous systems, the electrochemistry should, in theory, be refreshingly simple; the electrolyte takes no part in the reaction except for conveying the electroactive lithium ions during discharge from a high energy state in the negative electrode to a low energy state in the positive electrode while the electrons pass through the external circuit with a release of energy. The opposite reaction occurs on charge, so that rechargeability depends on the reversibility of the reactions at the electrodes.
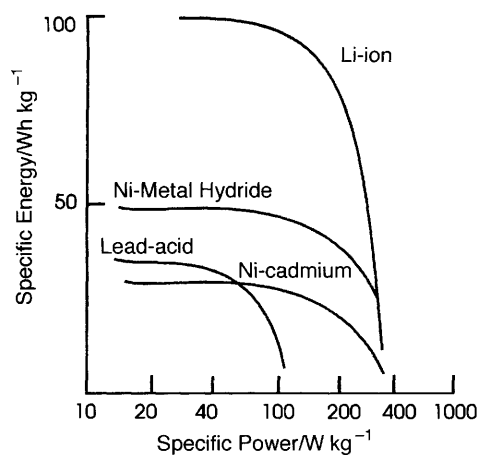
Fig. 1 A Ragone plot of energy and power density for various battery systems, showing the deterioration of energy density with increasing power demand

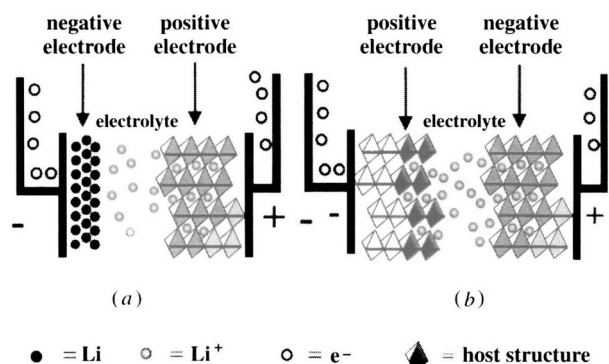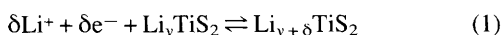● = Li   ○ = Li⁺   ○ = e-   ◆ = host structure

Fig. 2 Schematic diagrams of (a) a lithium cell, with a lithium metal negative and an insertion positive electrode, (b) a lithium ion cell which exchanges lithium between two insertion electrodes

At the positive electrode, reversibility is a consequence of the use of an insertion electrode material.[2] This is a solid which can incorporate the electroactive material into a solid solution with a wide stoichiometry range as in the example of titanium disulfide [eqn. (1)].

$$\delta \text{Li}^+ + \delta e^- + \text{Li}_y\text{TiS}_2 \rightleftharpoons \text{Li}_{y+\delta}\text{TiS}_2 \qquad (1)$$

The electrode undergoes a reversible topotactic redox reaction, meaning that the electrode material acts as a host structure which accommodates guest ions and electrons without destruction of the lattice. Many compounds have been selected for the positive insertion electrode and these will be reviewed below.

A second type of lithium cell, the lithium ion or rocking-chair cell is shown schematically in Fig. 2(b). Here the negative electrode is also composed of an insertion electrode, with advantages of dimensional stability and improved chemical stability as detailed in a later section. No lithium metal need exist in this cell—the lithium is always held as a guest in one of the electrodes depending on the state of charge. However, the specific charge is decreased, although the overall specific energy obtained is still impressive and an excellent cycle life may be obtained.

The literature on lithium batteries is already extensive, and the reader may find more detailed information in a recently published book on lithium batteries,[3] a more general handbook of batteries,[4] and a series of lithium battery conference proceedings.[5]

2 Theory

In the following sections we shall review some candidate materials with reference to the properties which are required for high energy and high power.

2.1 The cell potential

The maximum available energy is simply the free energy of reaction, ΔG. Therefore, high energy is a consequence of the choice of electrode materials. In the ideal case where there are no energy losses, the cell potential can be defined as in eqn. (2),

$$E = (\mu_{\text{Li}}^{\text{negative electrode}} - \mu_{\text{Li}}^{\text{positive electrode}})/F \qquad (2)$$

where μ'_{Li} indicates the values of the chemical potential of lithium metal at the electrode surfaces and F = Faraday's constant, 96 500 C mol⁻¹.

From the point of view of maximising the cell potential, lithium metal as the negative electrode with $\mu_{\text{Li}} = 0$ is of course the best choice. In the lithium ion cell, small negative values of μ_{Li} can be obtained using host materials where lithium exists at an activity close to that in the metallic state, e.g. graphite, for which the electrode potential is no more than 0.25 V positive with respect to lithium metal over the range $0.1 < y < 1$ for Li_yC_6. Conversely, in a positive electrode a highly negative value of μ_{Li} is obviously desirable so that a highly oxidising host is required. Lithium nickel oxide, Li_yNiO_2, has a stoichiometry range of $0 < y < 1$ with an electrode potential of between 4.2 and 3.5 V vs. lithium metal. Therefore, with a suitable choice of both materials, a minimum cell potential of about 3 V at the end of discharge is obtainable.

2.2 Theoretical cell capacity and specific energy

The theoretical cell capacity in A h g⁻¹ or A h cm⁻³ can be estimated from the stoichiometry ranges and molar masses of the electrode materials. Thus LiC_6 and Li_xNiO_2 are each required in quantities of about 80 g per Faraday of charge stored as compared with only 7 g of lithium metal. The theoretical maximum capacities of the Li/NiO_2 and $\text{LiC}_6/\text{NiO}_2$ cells are therefore about 300 A h kg⁻¹ and 170 A h kg⁻¹ respectively. With a useful cell potential of 3 V the specific energies become 880 W h kg⁻¹ and 500 W h kg⁻¹.

2.3 Power losses in the electrolyte

High power requires fast transport of lithium ions, which involves energy losses at several points in the cell. The most obvious loss is the Ohmic loss in the electrolyte, which is
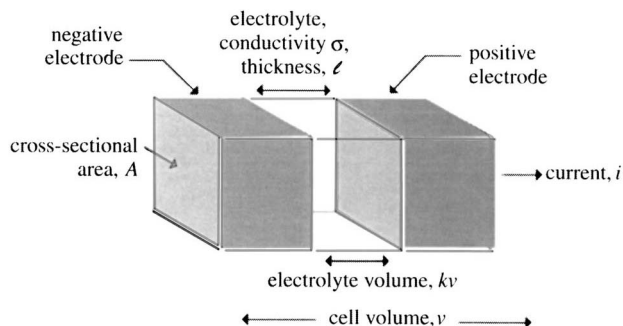

Fig. 3 Calculation of the Ohmic loss in the electrolyte according to eqn. (3)

calculated here for the cell shown in the scheme of Fig. 3 [eqn. (3)], where i = the cell current; l = the electrolyte thickness; A

$$\Delta V(\text{ohmic loss}) = iR = il/A\sigma = (i/vk)\ l^2/\sigma \qquad (3)$$

= the cross-sectional area of the electrolyte perpendicular to the current path; σ = the electrolyte conductivity; k = the ratio of the separator electrolyte volume to the cell volume; v = the cell volume.
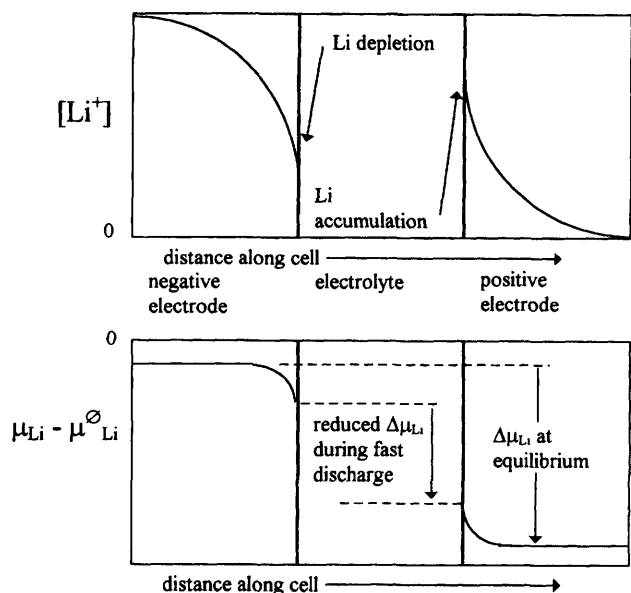
Fig. 4 Concentration polarisation of the electrodes is a consequence of changes in the surface concentrations of lithium during discharge. The difference between the chemical potentials of lithium at the two electrode surfaces, $\Delta\mu_{Li}$, determines the cell potential according to $V = \Delta\mu_{Li}/F - iR_{electrolyte}$.

The power density, P_v is obtained by multiplying the current per unit cell volume by the cell voltage, V [eqn. (4)].

$$P_v = V(i/v) = Vk\sigma\Delta V/l^2 \tag{4}$$

Taking, for example, $V = 3$ V, $k = 0.3$, $\sigma = 3 \times 10^{-4}$ S cm^{-1}, $\Delta V = 0.1$ V, $l = 0.01$ cm, we would have $P_v = 300$ W dm^{-3}. The calculation emphasises the needs for a high conductivity and minimisation of the electrolyte thickness as far as possible.

2.4 Concentration polarisation in the electrode

Discharge at a finite rate causes depletion of lithium at the surface of the negative electrode and accumulation at the positive electrode as shown in Fig. 4. Since it is the composition of the surface of the electrodes which determines the cell potential, the concentration changes can result in premature discharge if the concentration gradients become large. The temporary loss in cell potential due to the difference between the surface and average compositions of the electrodes is termed concentration polarisation. The effect can only be relieved by efficient transport of lithium in the electrodes.

Lithium transport in the electrodes has generally been treated as simple diffusion in a homogeneous phase. The minimum time taken for the discharge of a single electrode at constant potential (vs. a reference electrode) can be estimated from eqn. (5),[6] where M_0 is the initial lithium content; M_t is

$$\frac{M_t - M_0}{M_\infty - M_0} \approx 1 - \frac{8}{\pi^2}\exp\left\{\frac{-D\pi^2 t}{4l^2}\right\} \tag{5}$$

the amount of lithium in the electrode at time t; M_∞ is the amount of lithium in the electrode at equilibrium; D is the diffusion coefficient of lithium; l is the electrode thickness.

A 90% discharge would be obtained, for example, in a time $\tau = 0.85 \, l^2/D$.

Diffusion coefficients of lithium in pure electrode materials vary by many orders of magnitude, and much early work emphasised the need for insertion electrodes with diffusion coefficients of the order 10^{-8} cm^2 s^{-1} in order that electrodes of about 0.01 cm thickness could be discharged in about one hour.

2.5 Porous and composite electrodes

In reality, electrodes are formed into porous microcrystalline structures which can be permeated by a liquid electrolyte or formed into composite electrodes by blending with a polymer electrolyte[7] (Fig. 5). In these circumstances, problems due to
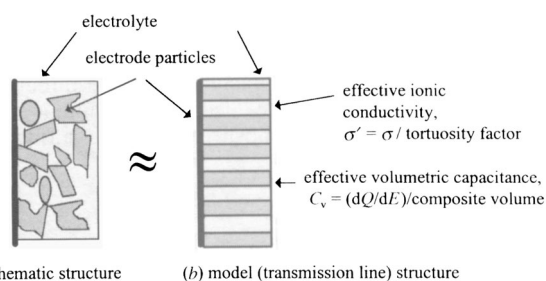

(*a*) schematic structure   (*b*) model (transmission line) structure

Fig. 5 (*a*) A composite electrode structure reduces the length of the diffusion path within the electrode material to about half the particle radius. Mass transport is provided by the interpenetrating electrolyte. (*b*) An effective diffusion coefficient for the structure is given by σ'/C_v.

concentration gradients within the electrode particles themselves can be alleviated by reducing the particle size, typically to 10–50 μm in diameter. The problem which remains is equalisation of concentration across the electrode thickness, which generally occurs by lithium ion conduction and diffusion in the intergranular electrolyte phase. Although the electric potential, ϕ, is almost constant in the regions which have a good electronic conductivity, an electric field $\partial\phi/\partial x$ exists in the intergranular electrolyte because of the gradient in the interfacial potential arising from a gradient in lithium chemical potential in the surrounding electrode grains [eqn. (6)].

$$\partial\phi/\partial x = -(\partial\mu_{Li}/\partial x)/F \tag{6}$$

Provided that the particle size is sufficiently small the effective diffusion coefficient may be shown to be given by eqn. (7),

$$D = \sigma'/C_v \tag{7}$$

where σ' is the effective ionic conductivity due to the electrolyte in the composite and C_v is the pseudocapacitance per unit volume of electrode material as shown by the equilibrium variation of electrode potential with inserted charge per unit volume [eqn. (8)], where $v_{electrode}$ is the electrode volume.

$$C_v = (dE/dQ)^{-1}/v_{electrode} \tag{8}$$

As an example, the value for the pseudocapacitance can be estimated for a non-graphitic carbon composite electrode; assuming a capacity of 1000 C cm^{-3} available over a potential range of, say 1 V, we obtain a capacitance of 1000 F cm^{-3}.

The effective ionic conductivity is reduced from the value for the electrolyte according to the volume fraction and another factor due to the tortuous conduction path. With an effective ionic conductivity of 10^{-5} S cm^{-1} the effective diffusion coefficient for the composite electrode would be around 10^{-8} cm^2 s^{-1}.

The above calculation emphasises the need for a highly conducting electrolyte within the electrode regions as well as the interelectrode gap. It also shows that high power density also requires a laminate structure with electrodes as thin as 0.01 cm.

To conclude this section, the estimations above may be related to the Ragone plot of Fig. 1. Lithium batteries may be expected to reach above 200 W h kg^{-1} and 100 W kg^{-1} provided the following conditions are met:

- an electrode couple with a potential difference of at least 3 V throughout discharge;
- electrode materials with (molar) masses below 100 g per Faraday of charge stored;
- electrolyte conductivity at least 3×10^{-4} S cm^{-1};
- a thin laminate structure with electrode and electrolyte thicknesses around 0.01 cm.

3 Non-aqueous electrolytes

3.1 Some alternative approaches

A prime consideration for an electrolyte in a battery is chemical stability to both the electrodes in the charged state. With a lithium electrode this is a difficult problem, although in some rare cases thermodynamic stability in contact with metallic lithium is indeed possible, e.g. the lithium halides. One of the first lithium cells to be manufactured was the lithium–iodine pacemaker cell in which the electrolyte, lithium iodide, is formed *in situ* at the iodine positive electrode surface during discharge [eqn. (9)].

$$2Li^+ + 2e^- + I_2 \rightarrow 2LiI \qquad (9)$$

Although this is an ingenious scheme for the prevention of self discharge, lithium iodide is a brittle solid at room temperature and has a low conductivity, about 10^{-7} S cm^{-1}. In order to achieve useful rates of discharge in the commercial device[8] the lithium surface is first coated with poly(2-vinylpyridine) to increase the conductivity of the lithium iodide, once formed, to a maximum of about 10^{-3} S cm^{-1}. Even so the applications of this cell are limited to those requiring very low discharge rates, so that rechargeability is not required.

A high temperature rechargeable cell has been developed based on molten lithium aluminium chloride as the electrolyte.[9] Because the melting point of the salt is higher than that of lithium metal, a lithium–aluminium alloy is used as the negative electrode. The insertion electrode FeS_2 is used as the positive electrode, so that the cell reaction is given by eqn. (10).

$$LiAl + FeS_2 \rightarrow LiFeS_2 + Al \qquad (10)$$
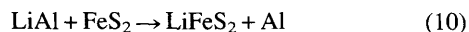
Solid electrolytes other than LiI have also been considered. For example, a lithium conducting glass has been used as the electrolyte in a small thin film cell.[10] However, a general problem with brittle solid electrolytes is that on cycling large strains occur at the electrode–electrolyte interface which cause disintegration of the structure if the film thickness exceeds a few μm.

3.2 Organic solvents

Most viable rechargeable lithium cells resort to electrolytes which are composed of solutions of appropriate lithium salts in organic solvents which are liquid at room temperature. The solvent should be aprotic, as active protons react with lithium to give hydrogen gas, e.g. acids and alcohols are prohibited [eqn. (11)].

$$2ROH + 2Li \rightarrow 2ROLi + H_2 \qquad (11)$$
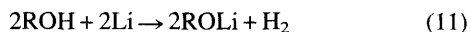
No organic solvents have been reported to be thermodynamically stable against lithium metal. However, varying degrees of kinetic stability have been reported in aprotic solvents.

In addition to stability, a high conductivity is required, which means that lithium ions must be mobilised in solution and separated from associated anions. Hydrocarbons, although quite stable to lithium, can neither dissolve nor dissociate lithium salts effectively—these properties require groups which can solvate the lithium ion (a Lewis acid) through the acid–base reaction in eqn. (12).

$$Li^+X^- + n(\text{Solvent}) \rightarrow Li^+ (\text{Solvent})_n + X^- \qquad (12)$$
$$\text{Lewis base}$$
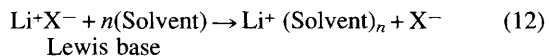
The solvent basicity may be quantified by the donor number.[11] A high relative permittivity also aids the separation of ion pairs. As well as a high degree of salt dissolution and dissociation, a low viscosity is also required for high conductivity. Some values of these properties for common solvents are given in Table 1.

After more than 25 years of study, involving many linear and cyclic ethers, linear and cyclic alkyl carbonates and other esters, a few systems have emerged as having the optimum combination of high conductivity, stability, low viscosity, low cost and

low toxicity. Suitable mixtures can be made which combine the favourable properties of the constituents and modifications can be made to suit particular system requirements such as low-temperature operation.

3.3 New lithium salts

The choice of lithium salt is also important. Early work centred on lithium perchlorate as a salt which dissociated readily and showed surprisingly good kinetic stability against lithium metal. Unfortunately, however, certain conditions led to unpredictable and catastrophic breakdown with explosive consequences in prototype batteries so that perchlorates are now avoided in most products destined for public use. Substitute salts have been found in the hexafluoroarsenate and hexafluorophosphate, which form solutions with conductivities around 10^{-3} S cm^{-1}. The former is now regarded as being too toxic for general use whereas the latter has been, at least temporarily, accepted despite problems of stability against dissociation into LiF and PF_5.

The continuing search for stable and easily dissociated salts has promoted research into new anions based on perfluoroalkanesulfonates. The first of these, lithium trifluoromethanesulfonate, abbreviated to lithium triflate, gave modest properties and is now challenged by specifically designed salts such as the 'TFSI' and 'methide' salts.
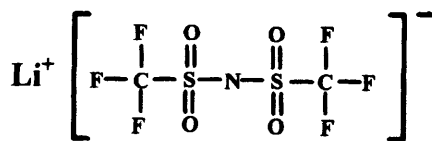
Li TFSI
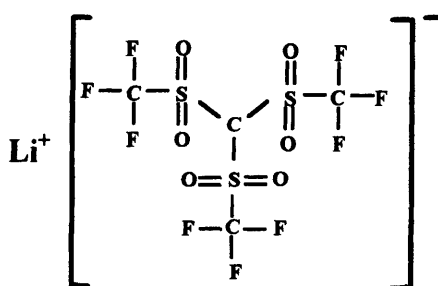
Li Methide

3.4 Polymer electrolytes

A liquid electrolyte must be contained in a porous solid or elastomeric separator which prevents direct contact between the electrodes. A stack pressure is generally applied to ensure good interparticle contact within the electrode material while dimensional changes in the electrode particles occur during cycling. Problems arise because separators containing liquid electrolytes

Table 1 Properties of some organic solvents used in electrolytes[12]

Solvent	Mp, t/°C	Relative permittivity, ε	Donor number	Viscosity/CP
2-Methyltetrahydrofuran	−137	6.2	18	0.47
Diethyl carbonate	−43	2.8	15	0.75
Diethyl ether	−116	4.3	19	0.24
Hexamethylphosphoric triamide	7	30	39	3.2
Ethylene carbonate	36	95	16	1.9 (at 36 °C)

tend to dry out, particularly with gas evolution during the first cycle. Containment of the liquid electrolyte in a separator can also cause problems due to non-uniformities in the stack pressure and the current path.

The problems of mechanical mobility in electrolytes are offered a solution through the use of polymer electrolytes with elastomeric qualities. Armand[13] described two ways in which elastomeric and electrolytic properties could be combined. The first and most elegant method was to introduce a solvating character into the polymer molecule. Poly(ethylene oxide), PEO, also named poly(oxyethylene), was found to solvate most metal salts with easily dissociatable anions to form elastomeric solutions with conductivities up to 10^{-4} S cm^{-1} above the melting point of 65 °C.

The field of polymer electrolytes has developed extensively since Armand's first work and polymeric solutions with lower melting points have been subsequently found by the depression of melting point and suppression of crystallisation using the following strategies:

● use of high concentrations of salts with large anions, e.g. Li TFSI;
● randomisation of chain sequences by introduction of oxymethylene units;[14]
● introduction of solvating groups into the side chains of low melting and low glass transition polymers such as poly-(phosphazene);[15]
● addition of liquid plasticisers;[16]
● cross-linking, which also improves mechanical strength.[17]

Considering that one of the major advantages of a polymer electrolyte is that it presents a mechanically stable barrier between the electrodes, some efforts have concentrated on the second type of conducting elastomer suggested by Armand, the gelled polymer electrolyte. This is essentially a liquid electrolyte of the type described above which is immobilised in a polymer matrix which does not necessarily have inherent solvating properties.

Another important area under development is that of polymer electrolytes having a transference number of one for the lithium ion. Progress in this direction has been made by binding the counterion to the polymer chain. However, the conductivities obtained are disappointingly low, possibly because the triple ions and higher aggregates which are normally responsible for high conductivities in liquid electrolytes are also immobilised in this approach.

4 Positive electrode materials

4.1 Models for the electrode potential

It has already been stated that the potential of an insertion electrode with respect to lithium metal is $-\mu_{Li}/F$. The value of the chemical potential of lithium may be written in terms of the chemical potentials of its constituents, the lithium ion and the electron [eqn. (13)].

$$\mu_{Li} = \mu_{Li^+} + \mu_{e-} \tag{13}$$

The two terms are illustrated in Fig. 6. The first term represents solvation of the lithium ion by the host lattice. A Lewis base character of the environment of the lithium ions, as provided by an oxide lattice, for example, is advantageous here. However a greater variation over different materials is caused by the electronic term which contributes to a negative chemical potential through a large negative energy E_F of an electron at the Fermi energy, with respect to the vacuum level [eqn. (14)].

$$\mu_e{}^{-Host} - \mu_e{}^{-Li} = F\ (E_F{}^{Host} - E_F{}^{Li}) \tag{14}$$

In qualitative chemical terms this simply means the electrode should be a strong oxidising agent. As the cell discharges, the average concentration of lithium in the positive electrode increases. Two contrasting situations are shown in Fig. 7. In the first case shown in Fig. 7(a), lithium is inserted to form a single-
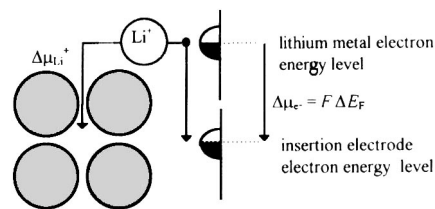
Fig. 6 Ionic and electronic contributions to the electrode potential. $\Delta\mu_{e-}$ depends mainly on the Fermi energy of host structure, whereas $\Delta\mu_{Li^+}$ varies with lithium ion site occupancy according to $\mu = \mu^\theta + ky + RT\ln [y/(y_{max} - y)]$ (see text).

phase solid solution so that the electrode potential falls gradually as the chemical potentials of both ions and electrons are increased. However, within the phase stability region the increase in Fermi energy due to electron population is largely compensated by a lowering of the band energy due to screening of the nuclear charge.[18] The most significant change in the equilibrium potential with composition is therefore due to the change in the chemical potential of the lithium ions [eqns. (15), (16)], where E^0 and μ^θ are standard potentials due to the

$$\mu = \mu^\theta + ky + RT\ln [y/(y_{max} - y)] \tag{15}$$

$$E = E^0 - ky/F - RT/F \ln [y/(y_{max} - y)] \tag{16}$$

guest–host interaction, y_{max} is the maximum value of y allowed by the number of available lattice sites; k represents the repulsion between lithium ions in close proximity, $R \ln [y/(y_{max})]$ is the configurational entropy of the inserted ions. (The configurational entropy term applies only to the ions if electrons are delocalised; a similar term for electrons may be added in the case of localised electronic states).

The simple model breaks down when the electron energy levels are almost filled and a new level or band must be occupied, or when the given lithium ion sites are almost filled, and an alternative structure becomes energetically favourable. In this case [Fig. 7(b)] the inserted lithium is partitioned between two phases. The discharge then proceeds by growth of the concentrated phase and a near-equilibrium discharge occurs at an almost constant potential until one phase is consumed.

4.2 Estimations of electrode capacity

Whether discharge occurs via a single phase or a succession of phases, the capacity of an electrode over an acceptably small potential range has been estimated as follows for ternary transition metal compounds Li_yMX_n.[19] The following assumptions were made:

● the oxidation state of the host metal changes by no more than one;
● the anions, X, are close-packed to give one octahedral cation site per anion. In this case the guest ion sites for Li$^+$ are the octahedral sites which remain after occupation by M.
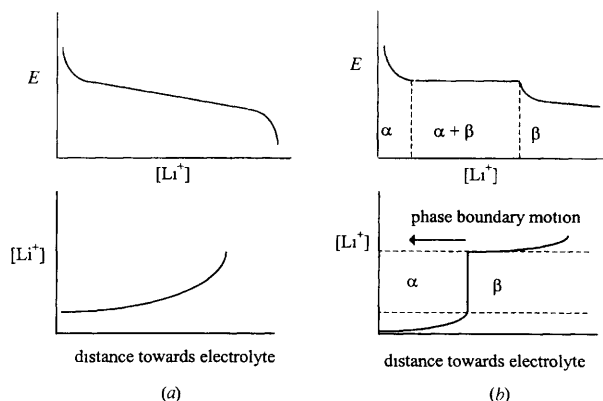
Fig. 7 Near-equilibrium potential–composition relation and composition–distance profiles (schematic) during discharge of a positive electrode: (a) without and (b) with phase conversion on insertion

Following this argument it may be seen that MX has no available sites for lithium and therefore has no reversible capacity. Discharge occurs via destructive phase transformation to give the metal and a binary lithium compound [e.g. eqn. (17)].

$$2Li + CuO \rightarrow Li_2O + Cu \qquad (17)$$
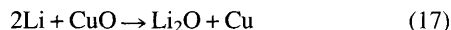
MX$_3$ would seem to have a high capacity due to the large number of vacant octahedral sites; however, the formation of Li$_2$MX$_3$ requires a double oxidation state change with a correspondingly high reduction in potential over the discharge range. Also, at high ratios of lithium to the transition metal, the structure can become unstable with respect to the irreversible precipitation of the binary lithium compound [e.g. eqn. (18)].

$$LiMX_3 + 2Li \rightarrow Li_2X + LiMX_2 \qquad (18)$$
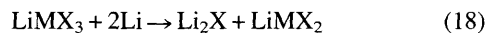
The maximum specific capacity (stored charge/mass) is therefore expected for MX$_2$ where reversible insertion reactions may occur according to eqn. (19).

$$yLi + MX_2 \rightleftharpoons Li_yMX_2 \; (0 < y < 1) \qquad (19)$$
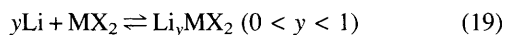
The argument presented above seems to hold for the smaller transition metal oxides which are well described by oxide close packing. However, capacities greater than one lithium per transition metal have been reported for layered and open framework structures. For example, the hexagonal phase of WO$_3$, stabilised by a small amount of added sodium oxide, has been reported to accommodate up to 2 Li per W.[20] Unfortunately, the additional capacity is of limited value because the potential decreases to below 2 V as the oxidation state of W approaches +4. Nevertheless, this finding challenges the general assumptions made above.

To maximise the potential of a positive electrode the electron energy must be considered. Generally, a low Fermi energy requires a very high oxidation state of an early transition metal, e.g. V^{5+}, or a moderate oxidation state of a late transition metal, e.g. Ni^{4+}, where poor d-electron screening of the nucleus increases the effective positive charge.

4.3 Inorganic electrodes designed for high energy
Titanium disulfide was one of the first compounds suggested for use as a lithium insertion electrode. Although insertion proceeds at rather low potentials, between 2.4 and 1.8 V vs. lithium metal, its redeeming features include:

- a good electronic conductivity over the range $0 < x < 1$ in Li$_x$TiS$_2$;
- a high diffusion coefficient for lithium ions;
- a reasonably low mass and volume per Faraday of charge stored;
- an excellent reversibility of lithium insertion.

A substitution of a later transition metal for Ti and an increase in the oxidation state may be expected to increase the potential. However, a consideration of the electron energy levels involved shows that high oxidation states of the metal cannot be accessed without oxidation of the sulfide ion to disulfide, higher sulfides and eventually sulfur.

In the case of a transition metal oxide, however, very high oxidation states of the metal can be achieved where the Fermi energy is highly negative. However, a thermodynamic limitation occurs due to the possibility of oxygen evolution by oxidation of the oxide ion. The equilibrium reaction of lithium in solution in the ternary oxide with oxygen gas can be written as in eqns. (20), (21).

$$2Li(MO_2) + \tfrac{1}{2} O_2 \rightleftharpoons Li_2O \qquad (20)$$
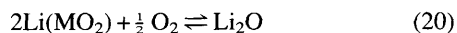
$$\Delta G = \Delta_f G^0 (Li_2O) + \mu(Li_2O) - 2\,\mu(Li) - \tfrac{1}{2}\mu(O_2) \qquad (21)$$

where $\qquad \Delta_f G^0 (Li_2O) = ca. - 600 \text{ kJ mol}^{-1}$

At equilibrium, $\Delta G = 0, \mu(O_2) = 0$ and $\mu(Li) = 0.5 \,\mu(Li_2O) + 0.5\Delta_f \,G^0(Li_2O)$.

This equation means that given an almost continuous distribution of electron energy states and lithium sites, the minimum potential, corresponding to saturation with Li$_2$O, would be about 3.1 V. The additional potential available in an unsaturated case can be estimated by realising that the change in $\mu(Li_2O)$ during insertion is mainly due to the Li$^+$–Li$^+$ repulsion term ky. This varies typically by about 0.5 V over the range $0 < y < 1$ in simple compounds and hence the potentials of such oxides approach 3.6 V for low y values.

An ingenious method of simultaneously raising the electrode potential beyond the thermodynamic prediction and increasing the discharge capacity is via synthesis of a precursor to the electrode material in the discharged state, followed by electrochemical extraction of lithium[21] at low temperature, where the electrode may be kinetically stable against oxygen loss. This was reported for Li$_y$CoO$_2$, which is currently used as the positive electrode in a commercial cell. The precursor is synthesised by high temperature reaction of the two carbonates to form LiCoO$_2$. Charging the electrode in situ within a cell gives a positive electrode with a specific capacity of up to 200 mA h g^{-1}, corresponding to the stoichiometry Li$_{0.3}$CoO$_2$. At this point the potential vs. a lithium electrode would be about 4.5 V, where parasitic reactions of electrolyte oxidation become excessive and prevent further extraction of lithium. Lithium nickel oxide and lithium cobalt–nickel oxides have been shown to have a greater stoichiometry range due to slightly lower potentials for lithium extraction. It should be noted that this route would give greater scope for the improvement of energy density if new electrolytes could be found to withstand the highly oxidising conditions on charge.

The same principle as that described above has been used to synthesise the spinel-related Li$_y$Mn$_2$O$_4$ electrode.[22] In this material the value of y can be reduced from one, as prepared, to almost zero because the potential is lower, about 4.15 V. Because the lithium–transition metal oxide ratio is smaller in this case the specific energy is correspondingly smaller. LiMn$_2$O$_4$ can also be reduced electrochemically to Li$_2$Mn$_2$O$_4$. In this case the reaction involves an abrupt phase change at a constant potential of about 3 V.

4.4 Organic electrodes
Conducting polymers have also been considered as positive electrodes for lithium batteries. Polypyrrole, in combination with a graphite negative electrode, was recently shown[23] to give a cell with a specific energy of 300 W h kg^{-1}.

Poly(carbon disulfide), PCS, has been reported to give a specific capacity approaching 1000 A h kg^{-1} when used as the positive electrode.[24] Although the average cell potential with metallic lithium electrodes was only 2 V, this gives an impressively high theoretical specific energy, close to 2000 W h kg^{-1}. However, a substantial capacity loss occurs on extended cycling.

5 Negative electrodes

5.1 Lithium metal
A negative electrode consisting of metallic lithium should be ideal from a consideration of the specific energy because of its small molar mass of 7 g mol^{-1}, theoretically providing almost 4 A h of charge storage per gram of material. However, complete reversibility of the negative electrode reaction, lithium dissolution and plating, is practically unobtainable because of corrosion and dendritic plating[25] which cause a decrease in the specific capacity and a safety hazard due to micronisation of the lithium (Fig. 8).

It is probably inevitable that some reaction occurs between lithium and any electrolyte which has a sufficiently high conductivity at room temperature. Kinetic stability thus exists due to a passivation layer of reaction products. Successful discharge is, however, possible because the passivation layer
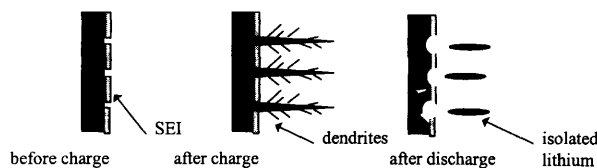
Fig. 8 Dendrite formation on a lithium electrode causes capacity loss by redistributing lithium from the bulk to isolated islands in the electrolyte

itself can have a sufficient conductivity to act as an auxiliary electrolyte layer, or solid electrolyte interface (SEI).[26]

Problems arise on charge, when a non-uniform current density causes the lithium to plate in a dendritic form, by-passing the original passivation layer and causing the deposition of a secondary passivation layer on the dendrites themselves. Further problems arise on the next discharge half-cycle, when some of the newly-plated lithium becomes isolated and full discharge can only be obtained by removing lithium from beneath the first passivation layer. The end result is a composite mass of finely divided lithium interspersed with the reaction products. Under these circumstances a significant corrosion of the lithium electrode occurs so that a large excess of lithium has to be used to compensate. Furthermore, the finely divided lithium is extremely reactive and presents a serious fire hazard especially when lithium dendrites cause a short-circuit.

The above problems do not, however, necessarily preclude the use of lithium metal as the negative electrode because it has been found that the quality of lithium plating reaction depends strongly on the electrolyte composition. Active research on the lithium metal negative electrode is still being pursued in many laboratories where the following approaches are used:

● the use of more inert solvent systems[27] and salts;[28]
● increasing the stack pressure on the electrode;[29]
● the addition to the electrolyte of compounds which improve the plating morphology;[30]
● the use of polymer electrolytes.[31]

5.2 Negative electrodes other than lithium metal

Lithium–aluminium alloys have already been mentioned as the negative electrode material in high temperature cells. These cannot be used at low temperature because of the very low diffusion coefficient of lithium in the α Al phase which forms on discharge. However, a number of other alloy negative electrodes have been proposed, which include Li_xSn, Li_xBi, and Li_xSi.

Graphite was one of the first known examples of an insertion electrode, with an ability to accept lithium up to a maximum stoichiometry of LiC_6, corresponding to a theoretical specific capacity of about 370 A h kg^{-1}. Fortunately for the lithium-ion battery, the electrochemical insertion of lithium occurs reversibly between 0.2 and about 0.05 V vs. lithium. Phase transitions due to increasing orders of lithium insertion between the graphene sheets have been observed by plateaux in the near-equilibrium discharge curve and in situ X-ray diffractograms taken during discharge[32] (Fig. 9).

Graphite insertion is often accompanied by side reactions involving electrolyte decomposition, enhanced by the large surface area compared with a metallic lithium electrode and, in extreme cases, exfoliation of the structure. Suitable choice of electrolyte reduces this problem by surface passivation during the first charge cycle. The situation is different from that of a plated lithium electrode because the dimensional changes are less and more evenly distributed—dendrite formation cannot occur. However, the additional charge required to form the passivating film is substantial, requiring the addition of excess positive electrode material and a consequent reduction in the energy density.

Non-graphitic forms of carbon have shown more efficient passivation, possibly because exfoliation is less likely in a cross-linked network structure. In the case of 'hard' carbons
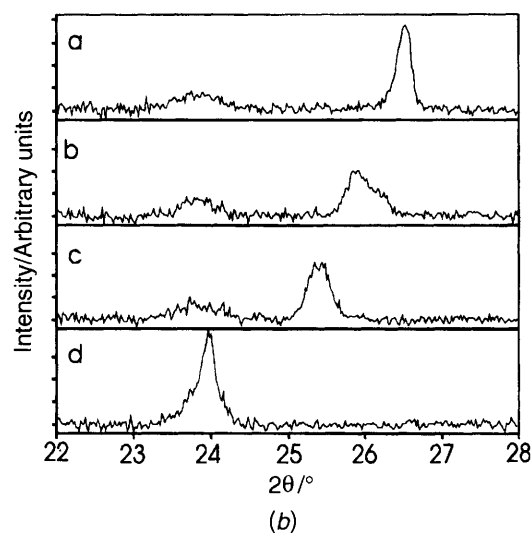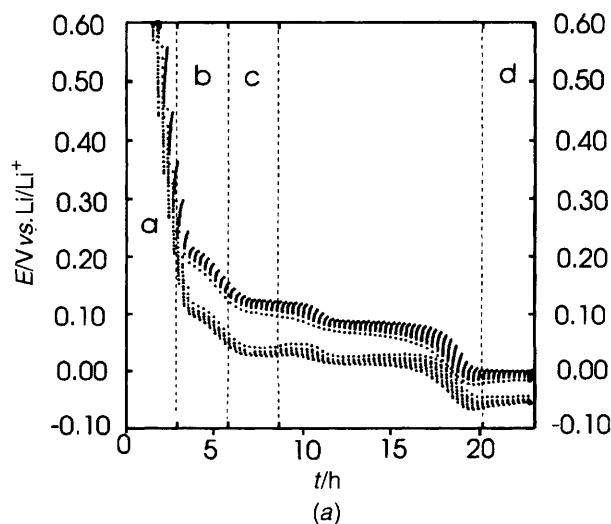

(a)

(b)

Fig. 9 (a) Discharge of a graphite electrode as observed by current-pulsed coulometric titration. Potentials in lower and upper curves correspond to 300 s periods during insertion (including iR and concentration polarisation) and 750 s relaxation, (near-equilibrium values) respectively. The time axis also represents the total inserted charge. (b) X-Ray diffractograms showing the position of the (002) peak, which reveals the various stages (phases) produced during lithium insertion.

such as various types of coke, however, discharge occurs over potential range between 0 and 1 V vs. lithium and the capacity is less than that of graphite. 'Soft' carbons are partially graphitised by heating above 2000 °C and heating to 2600 °C produces electrode materials with capacities approaching that of natural graphite.[33]

Carbons with capacities much higher than that of LiC_6 have been reported.[34] However, problems remain with irreversible capacity on first charge and the optimisation of the carbon negative electrode is under intensive investigation.

6 Current manufacturing technology and future prospects

A theoretical specific energy of 500 W h kg^{-1} was calculated for the LiC_6/NiO_2 cell. However, the specific energy of commercial lithium ion cells is presently around 110 W h kg^{-1} for the $C/LiCoO_2$ system.[29] This is partly due to the chemistry—electrolyte instability prevents full extraction of lithium from the positive electrode, and requires the addition of excess $LiCoO_2$ to provide for the initial passivation of the negative electrode during the first charge. However, the remainder of the

shortfall is due to the packaging and the presence of additional components for fast and efficient extraction of electrochemical energy from the active materials.

Efficient current collectors are required to act as substrates for the electrode films and to carry the cell current to and from the electrodes. Since the mass and volume of these materials are included in the practical energy specifications, it is important that the current collectors are made in very thin film form and that they have sufficient strength to withstand stresses generated in the cell fabrication and in subsequent cycling. Metals are normally used, so that corrosion is an important issue, especially in view of the reactivity of the materials and extremes of electrochemical potential applied.

The negative electrode current collector must resist lithium insertion to form alloys, because alloy formation would deplete lithium from the electrode and also degrade the mechanical properties of the current collector. Thermodynamic data are a good guide in this case, and alloy phase diagrams can be used to find which metals have a low lithium solubility and no compound formation. Copper is a popular choice since it is relatively cheap, less harmful than nickel, highly conductive and easily rolled into thin foils.

The positive electrode current collector must be resistant to oxidation in the presence of the anion present in the electrolyte. This is a difficult condition to satisfy, since the potential of the positive electrode is usually above the dissolution potential of all the metals. Also, anions designed for high solubility and dissociation of their lithium salts usually form highly soluble salts with other metals. The same is true for the solvent—a high donor number stabilises not only lithium complexes, but metal salt complexes in general. Therefore a passivating film is essential for a metallic positive electrode current collector and aluminium has been chosen in the first generation of products.

Table 2, taken from data for a lithium ion cell,[35] shows the components of a lithium ion cell of the type shown in Fig. 10. The low thicknesses of the electrolyte and electrode layers are noteworthy, and contribute to a high power density.

Table 2 Typical design parameters for a $C/LiCoO_2$ cylindrical cell[29]

Function	Material	Thickness/ μm
Negative electrode active material	non-graphitised carbon	90 each side
Negative electrode current collector	copper	25
Positive electrode active material	$LiCoO_2$	80 each side
Positive electrode current collector	aluminium	25
Electrolyte/separator	$PC/DEC/LiPF_6/Celgard$	25

Improvements will be sought in the fabrication methods for materials already in use in order to increase the energy storage and power specifications, e.g. to give an important increase in charge rate which may be required in the electric vehicle application. The density of active material on the electrodes is presently far below the theoretical value because of the porosity required to accommodate electrolyte and possibly some decomposition products. Nanostructural and microstructural control of materials during synthesis and fabrication of electrodes are of obvious relevance here. A decrease in the laminate size may also contribute to high charge rates, as will control of the electrolyte path within the electrode composite.

Safety, cost and environmental acceptability are of paramount importance in the choice of the battery system and any associated materials. Thus carbon and manganese dioxide are considered to be important materials for lithium ion systems.

It is generally accepted that lithium itself is plentiful, e.g. in ocean water. Regarding other components, it is easy to estimate the costs of simple materials according to the presence of any
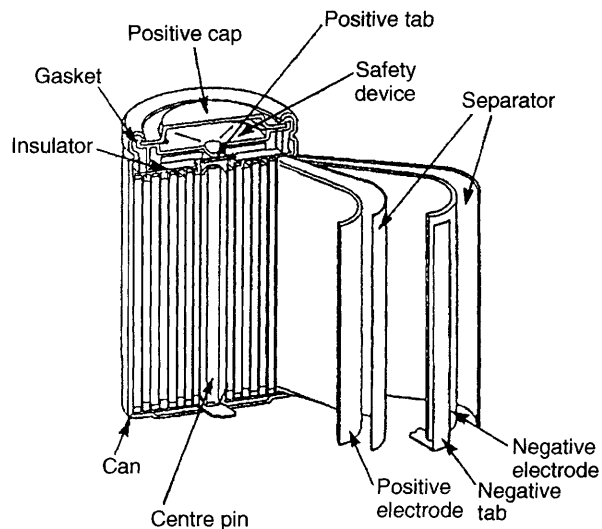
Fig. 10 Schematic construction of a typical cylindrical-type lithium cell

rare elements, but it is difficult to estimate the ultimate cost of a speciality chemical in tonnage quantities. Therefore changes in the choice of materials can be expected with the discovery of a cheap synthetic methods.

Polymer electrolytes should ultimately be superior to liquids for many reasons, including durability, safety, flexibility and ease of manufacture. Solvent-free polymers also offer the possibility of increasing the lifetime beyond the two years typically obtained at present. However, improvements in room temperature conductivity are required for high power.

In conclusion, it may be said that rechargeable lithium batteries are now well established and set to take over a large fraction of a rapidly expanding market. Projected specifications for future generation products are: 180 W h kg^{-1}, 360 W h dm^{-3} with a 500 cycle life, or more than 120 W h kg^{-1}, 240 W h dm^{-3} with a 3500 cycle life.[1] Given the appropriate investment in research and development, improvements in materials and cell design may be expected to continue for many decades ahead.

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