

Issues and challenges facing rechargeable lithium batteries

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Technological improvements in rechargeable solid-state batteries are being driven by an ever-increasing demand for portable electronic devices. Lithium-ion batteries are the systems of choice, offering high energy density, flexible and lightweight design, and longer lifespan than comparable battery technologies. We present a brief historical review of the development of lithium-based rechargeable batteries, highlight ongoing research strategies, and discuss the challenges that remain regarding the synthesis, characterization, electrochemical performance and safety of these systems

Rechargeable Li-ion cells are key components of the portable, entertainment, computing and telecommunication equipment required by today's information-rich, mobile society. Despite the impressive growth in sales of batteries worldwide, the science underlying battery technology is often criticized for its slow advancement. This is true whatever the technology considered (for example, nickel-cadmium, nickel-metal hydride or Li ion). Certainly, when compared, energy storage cannot keep pace with the rate of progress in the computer industry (Moore's law predicts a doubling of memory capacity every two years), yet the past decade has produced spectacular advances in chemistry and engineering within the emerging technologies of Ni-MeH and Li-ion batteries. These cells are now supplanting the well known Ni-Cd batteries.

A battery is composed of several electrochemical cells that are connected in series and/or in parallel to provide the required voltage and capacity, respectively. Each cell consists of a positive and a negative electrode (both sources of chemical reactions) separated by an electrolyte solution containing dissociated salts, which enable ion transfer between the two electrodes. Once these electrodes are connected externally, the chemical reactions proceed in tandem at both electrodes, thereby liberating electrons and enabling the current to be tapped by the user. The amount of electrical energy, expressed either per unit of weight (W h kg^{-1}) or per unit of volume (W h l^{-1}), that a battery is able to deliver is a function of the cell potential (V) and capacity (A h kg^{-1}), both of which are linked directly to the chemistry of the system. Among the various existing technologies (Fig. 1), Li-based batteries — because of their high energy density and design flexibility — currently outperform other systems, accounting for 63% of worldwide sales values in portable batteries¹. This explains why they receive most attention at both fundamental and applied levels.

Historical developments in Li-battery research

Before reviewing the present status of research and future challenges for Li-battery technologies, we present a brief historical account of developments over the past 30 years, as personally perceived.

The motivation for using a battery technology based on Li metal as anode relied initially on the fact that Li is the most electropositive (-3.04 V versus standard hydrogen electrode)

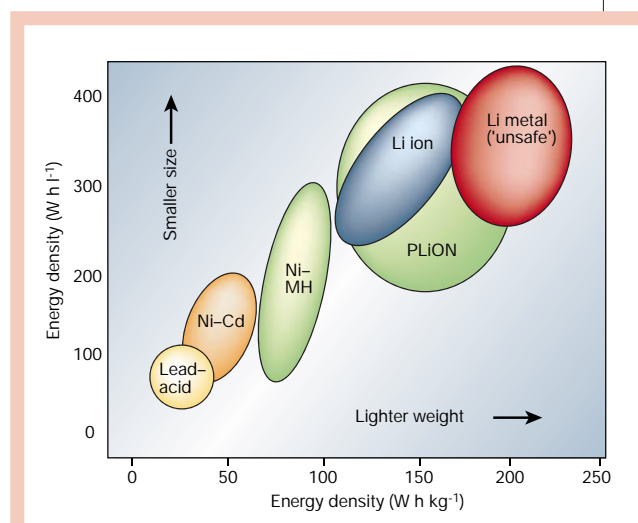


Figure 1 Comparison of the different battery technologies in terms of volumetric and gravimetric energy density. The share of worldwide sales for Ni-Cd, Ni-MeH and Li-ion portable batteries is 23, 14 and 63%, respectively. The use of Pb-acid batteries is restricted mainly to SLI (starting, lighting, ignition) in automobiles or standby applications, whereas Ni-Cd batteries remain the most suitable technologies for high-power applications (for example, power tools).

as well as the lightest (equivalent weight $M = 6.94 \text{ g mol}^{-1}$, and specific gravity $\rho = 0.53 \text{ g cm}^{-3}$) metal, thus facilitating the design of storage systems with high energy density. The advantage in using Li metal was first demonstrated in the 1970s with the assembly of primary (for example, non-rechargeable) Li cells². Owing to their high capacity and variable discharge rate, they rapidly found applications as power sources for watches, calculators or for implantable medical devices. Over the same period, numerous inorganic compounds were shown to react with alkali metals in a reversible way. The discovery of such materials, which were later identified as intercalation compounds, was crucial in the development of high-energy rechargeable Li systems. Like most innovations, development of the technology resulted from several contributions. By 1972, the concept of electrochemical intercalation and its potential use were clearly defined^{3,4}, although the information was not widely disseminated, being reported only in conference proceedings. Before this time, solid-state chemists had been accumulating

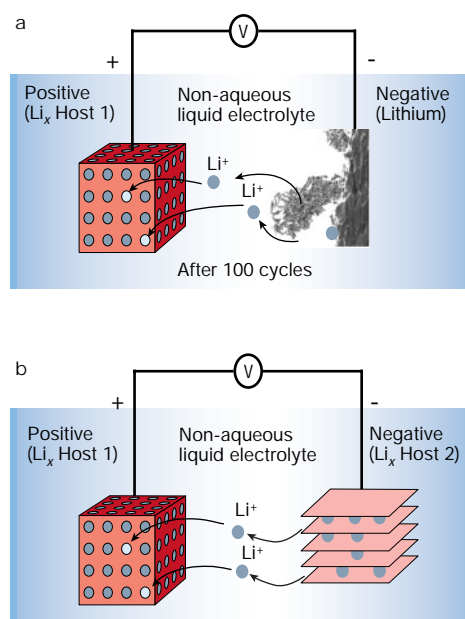


Figure 2 Schematic representation and operating principles of Li batteries. **a**, Rechargeable Li-metal battery (the picture of the dendrite growth at the Li surface was obtained directly from *in situ* scanning electron microscopy measurements⁷¹). **b**, Rechargeable Li-ion battery.

structural data on the inorganic layered chalcogenides^{5,6}, and merging between the two communities was immediate and fruitful.

In 1972, Exxon^{7,8} embarked on a large project using TiS_2 as the positive electrode, Li metal as the negative electrode and lithium perchlorate in dioxolane as the electrolyte. TiS_2 was the best intercalation compound available at the time, having a very favourable layered-type structure. As the results were published in readily available literature, this work convinced a wider audience. But in spite of the impeccable operation of the positive electrode, the system was not viable. It soon encountered the shortcomings of a Li-metal/liquid electrolyte combination — uneven (dendritic) Li growth as the metal was replated during each subsequent discharge–recharge cycle (Fig. 2a), which led to explosion hazards. Substituting Li metal for an alloy with Al solved the dendrite problem⁹ but, as discussed later, alloy electrodes survived only a limited number of cycles owing to extreme changes in volume during operation. In the meantime, significant advances in intercalation materials had occurred with the realization at Bell Labs that oxides, besides their early interest for the heavier chalcogenides^{10,11}, were giving higher capacities and voltages. Moreover, the previously held belief that only low-dimensional materials

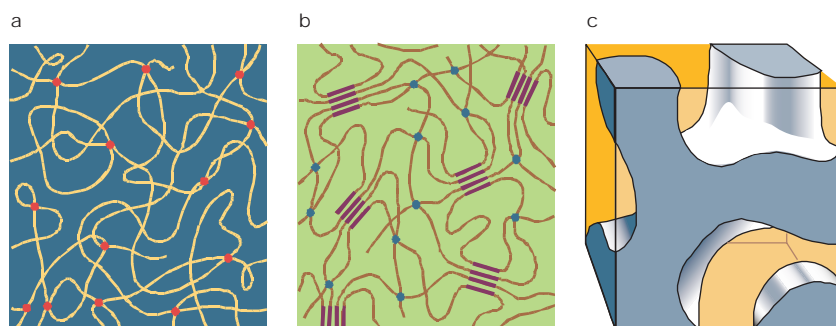
could give sufficient ion diffusion disappeared as a framework structure (V_6O_{13}) proved to function perfectly¹². Later, Goodenough, with Li_xMO_2 (where M is Co, Ni or Mn)^{13,14}, would propose the families of compounds that are still used almost exclusively in today's batteries.

To circumvent the safety issues surrounding the use of Li metal, several alternative approaches were pursued in which either the electrolyte or the negative electrode was modified. The first approach¹⁵ involved substituting metallic Li for a second insertion material (Fig. 2b). The concept was first demonstrated in the laboratory by Murphy *et al.*¹⁶ and then by Scrosati *et al.*¹⁷ and led, at the end of the 1980s and early 1990s, to the so-called Li-ion or rocking-chair technology. The principle of rocking-chair batteries had been used previously in Ni–MeH batteries^{18,19}. Because of the presence of Li in its ionic rather than metallic state, Li-ion cells solve the dendrite problem and are, in principle, inherently safer than Li-metal cells. To compensate for the increase in potential of the negative electrode, high-potential insertion compounds are needed for the positive electrode, and emphasis shifted from the layered-type transition-metal disulphides to layered- or three-dimensional-type transition-metal oxides¹³. Metal oxides are more oxidizing than disulphides (for example, they have a higher insertion potential) owing to the more pronounced ionic character of 'M–O' bonds compared with 'M–S' bonds. Nevertheless, it took almost ten years to implement the Li-ion concept. Delays were attributed to the lack of suitable materials for the negative electrode (either Li alloys or insertion compounds) and the failure of electrolytes to meet — besides safety measures — the costs and performance requirements for a battery technology to succeed. Finally, capitalizing on earlier findings^{20,21}, the discovery of the highly reversible, low-voltage Li intercalation–deintercalation process in carbonaceous material²² (providing that carefully selected electrolytes are used), led to the creation of the C/LiCoO₂ rocking-chair cell commercialized by Sony Corporation in June 1991 (ref. 23). This type of Li-ion cell, having a potential exceeding 3.6 V (three times that of alkaline systems) and gravimetric energy densities as high as 120–150 Wh kg^{−1} (two to three times those of usual Ni–Cd batteries), is found in most of today's high-performance portable electronic devices.

The second approach²⁴ involved replacing the liquid electrolyte by a dry polymer electrolyte (Fig. 3a), leading to the so-called Li solid polymer electrolyte (Li-SPE) batteries. But this technology is restricted to large systems (electric traction or backup power) and not to portable devices, as it requires temperatures up to 80 °C. Shortly after this, several groups tried to develop a Li hybrid polymer electrolyte (Li-HPE) battery²⁵, hoping to benefit from the advantages of polymer electrolyte technology without the hazards associated with the use of Li metal. 'Hybrid' meant that the electrolyte included three components: a polymer matrix (Fig. 3b) swollen with liquid solvent and a salt. Companies such as Valence and Danionics were involved in developing these polymer batteries, but HPE systems never materialized at the industrial scale because Li-metal dendrites were still a safety issue.

With the aim of combining the recent commercial success enjoyed by liquid Li-ion batteries with the manufacturing advantages

Figure 3 Schematic representations of polymer electrolyte networks. **a**, Pure (dry) polymer consisting of entangled chains, through which the Li ions (red points) move assisted by the motion of polymer chains. **b**, A hybrid (gel) network consisting of a semicrystalline polymer, whose amorphous regions are swollen in a liquid electrolyte, while the crystalline regions enhance the mechanical stability. **c**, A poly-olefin membrane (Celgard for instance) in which the liquid electrolyte is held by capillaries.



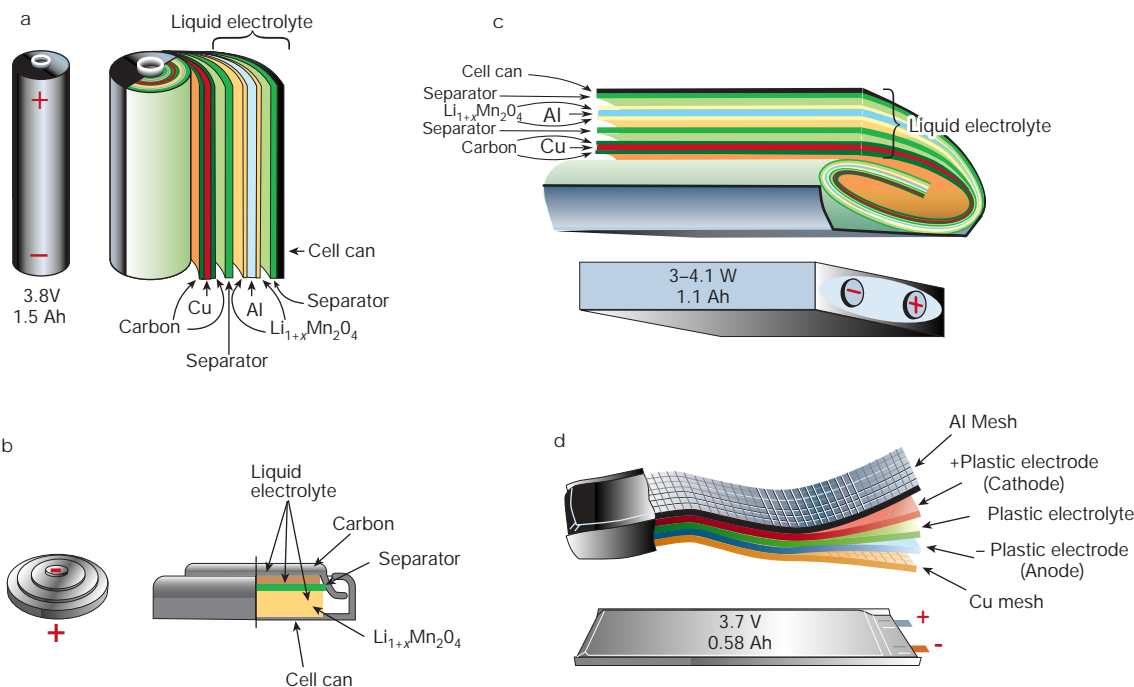


Figure 4 Schematic drawing showing the shape and components of various Li-ion battery configurations. **a**, Cylindrical; **b**, coin; **c**, prismatic; and **d**, thin and flat. Note the

unique flexibility of the thin and flat plastic LiION configuration; in contrast to the other configurations, the PLiION technology does not contain free electrolyte.

presented by the polymer technology, Bellcore researchers introduced polymeric electrolytes in a liquid Li-ion system²⁶. They developed the first reliable and practical rechargeable Li-ion HPE battery, called plastic Li ion (PLiON), which differs considerably from the usual coin-, cylindrical- or prismatic-type cell configurations (Fig. 4). Such a thin-film battery technology, which offers shape versatility, flexibility and lightness, has been developed commercially since 1999, and has many potential advantages in the continuing trend towards electronic miniaturization. Finally, the 'next generation' of bonded liquid-electrolyte Li-ion cells, derived from the plastic Li-ion concept, are beginning to enter the market place. Confusingly called Li-ion polymer batteries, these new cells use a gel-coated, microporous poly-olefin separator bonded to the electrodes (also gel-laden), rather than the P(VDF-HFP)-based membrane (that is, a copolymer of vinylidene difluoride with hexafluoropropylene) used in the plastic Li-ion cells.

Having retraced almost 30 years of scientific venture leading to the development of the rechargeable Li-ion battery, we now describe some of the significant issues and opportunities provided by the field by highlighting the various areas in need of technological advances.

Present status and remaining challenges

Whatever the considered battery technology, measures of its performance (for example, cell potential, capacity or energy density) are related to the intrinsic property of the materials that form the positive and negative electrodes. The cycle-life and lifetime are dependent on the nature of the interfaces between the electrodes and electrolyte, whereas safety is a function of the stability of the electrode materials and interfaces. Compared with mature battery technologies, such as lead-acid or Ni-Cd, rechargeable Li-based battery technologies are still in their infancy, leaving much hope for improvement over the next decade. Such improvements should arise from changes in battery chemistry and cell engineering. Advances in active chemistry are left to the solid-state chemists' creativity and innovation in the design and elaboration of new intercalation electrodes. At the same time, they must bear in mind that it is impossible to predict the demands

that might be placed on tomorrow's portable devices, which in turn places different requirements on the active material chemistry. For instance, with respect to the lower operating voltages of emerging electronics, much debate has focused on whether we should develop a low-voltage active chemistry or rely entirely on electronics (d.c.-d.c. converters) and persist in searching for high-voltage active Li chemistry. Finding the best-performing combination of electrode-electrolyte-electrode can be achieved only through the selective use of existing and new materials as negative and positive electrodes, and of the right electrolyte combination, so as to minimize detrimental reactions associated with the electrode-electrolyte interface — the critical phase of any electrochemical system.

Materials for positive electrodes

The choice of the positive electrode depends on whether we are dealing with rechargeable Li-metal or Li-ion batteries (Fig. 5)²⁷. For rechargeable Li batteries, owing to the use of metallic Li as the negative electrode, the positive electrode does not need to be lithiated before cell assembly. In contrast, for Li-ion batteries, because the carbon negative electrode is empty (no Li), the positive one must act as a source of Li, thus requiring use of air-stable Li-based intercalation compounds to facilitate the cell assembly. Although rechargeable Li-SPE cells mainly use Li-free V_2O_5 or its derivatives as the positive electrode, $LiCoO_2$ is most widely used in commercial Li-ion batteries, deintercalating and intercalating Li around 4 V.

Initially, the use of layered $LiNiO_2$ was considered²⁸, as this displayed favourable specific capacity compared with $LiCoO_2$. But expectations were dismissed for safety reasons after exothermic oxidation of the organic electrolyte with the collapsing delithiated Li_xNiO_2 structure. Delithiated Li_xCoO_2 was found to be more thermally stable than its Li_xNiO_2 counterpart. Thus, substitution of Co for Ni in $LiNi_{1-x}Co_xO_2$ was adopted to provide a partial solution to the safety concerns surrounding $LiNiO_2$.

Although the reversible delithiation of $LiCoO_2$ beyond 0.5 Li is feasible, delithiation for commercial applications has been limited to that value for safety reasons (charged cut-off limited to around

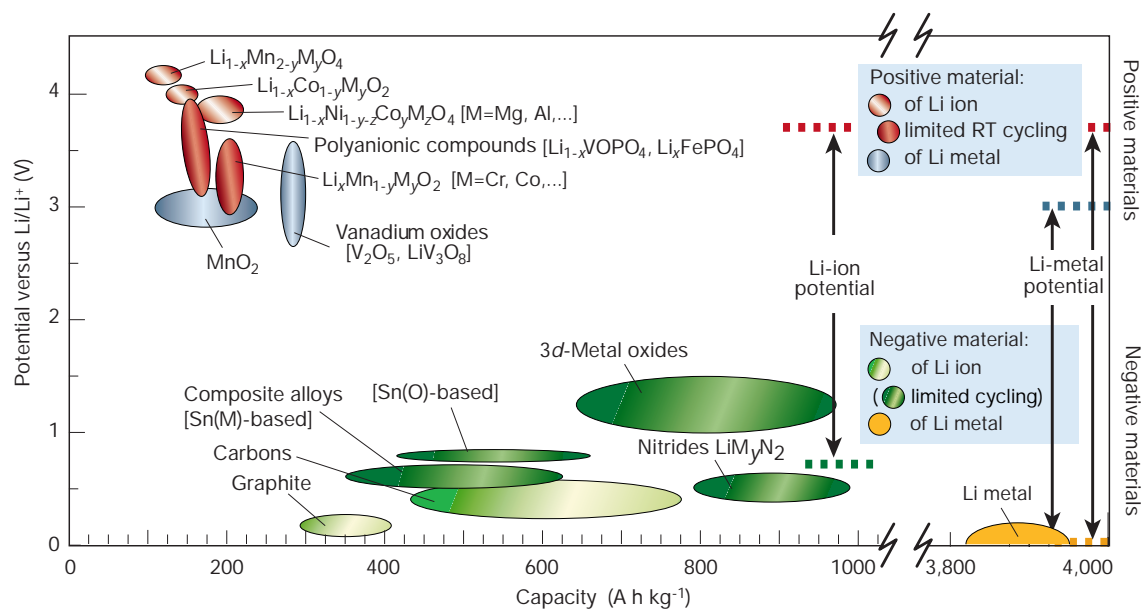


Figure 5 Voltage versus capacity for positive- and negative-electrode materials presently used or under serious considerations for the next generation of rechargeable Li-based cells. The output voltage values for Li-ion cells or Li-metal cells are

represented. Note the huge difference in capacity between Li metal and the other negative electrodes, which is the reason why there is still great interest in solving the problem of dendrite growth.

4.2 V). Several routes were investigated to circumvent these safety and capacity issues. Among them was the successful stabilization of the layered structural framework by an electrochemically inert di-, tri- or tetravalent cationic substitute for Ni or Co (Al, Ga, Mg or Ti). This led to $\text{LiNi}_{1-x}\text{Ti}_{x/2}\text{Mg}_{x/2}\text{O}_2$ phases²⁹, which were claimed to be safe and which displayed practical capacities of 180 mA h g^{-1} compared to only 140 mA h g^{-1} for LiCoO_2 . Another line of investigation involved the synthesis by *chimie douce* ('soft chemistry') of the layered LiFeO_2 and LiMnO_2 phases to take advantage of the $\text{Fe}^{4+}/\text{Fe}^{3+}$ and $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couples, respectively. In spite of the numerous and diverse synthesis methods, attempts to prepare electrochemically attractive LiFeO_2 phases failed. In contrast, research on LiMnO_2 has been more fruitful³⁰, and the structural instability of the layered phase reversing to the spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ upon cycling has recently been diminished through cationic substitution by chromium ($\text{Li}_{1+x}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_2$)³¹. These materials exhibit a capacity of 190 mA h g^{-1} (larger than that expected from the full oxidation of Mn^{3+} to Mn^{4+}) with little capacity fading upon cycling. It seems that within these materials, the role of Mn is to stabilize the layered structure of the chromium oxide, and that the large capacity is nested in the Cr oxidation state that changes reversibly from +3 to +6. It is therefore unfortunate that Cr presents major toxicity and pricing issues.

The spinel LiMn_2O_4 , although possessing $\approx 10\%$ less capacity than LiCoO_2 , has an advantage in terms of cost and is perceived as being 'green' (that is, non-toxic and from abundant material source). Additionally, it has long been recognized as a potential alternative cathode¹⁴. Its implementation has been delayed because of limited cycling and storage performances at elevated temperatures, although these hurdles were overcome recently by synthesizing dually substituted $\text{LiMn}_{2-x}\text{Al}_x\text{O}_{4-y}\text{F}_y$ spinel phases³², and by altering their surface chemistry³³.

In the search for improved materials for positive electrodes, it has been recognized recently that NaSICON (a family of Na super-ionic conductors) or olivine (magnesium iron silicate) oxyanion scaffolded structures (Fig. 6), built from corner-sharing MO_6 octahedra (where M is Fe, Ti, V or Nb) and XO_4^- tetrahedral anions (where X is S, P, As, Mo or W), offer interesting possibilities³⁴. Polyoxyanionic structures

possess M–O–X bonds; altering the nature of X will change (through an inductive effect) the ionic-covalent character of the M–O bonding. In this way it is possible to systematically map and tune transition-metal redox potentials. For instance, with the use of the phosphate polyanions PO_4^{3-} , the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{V}^{4+}/\text{V}^{3+}$ redox couples lie at higher potentials than in the oxide form. One of the main drawbacks with using these materials is their poor electronic conductivity, and this limitation had to be overcome^{35,36} through various materials processing approaches, including the use of carbon coatings, mechanical grinding or mixing, and low-temperature synthesis routes to obtain tailored particles. LiFePO_4 , for example, can presently be used at 90% of its theoretical capacity (165 mA h g^{-1}) with decent rate capabilities, and thus is a serious candidate for the next generation of Li-ion cells (Fig. 7). As expected in the light of these promising results, polyoxyanionic-type structures having XO_4^- entities (where X is Si, Ge) are now receiving renewed attention with respect to their electrochemical performance as electrode materials.

Although numerous classes of insertion–deinsertion materials were synthesized over the past 20 years, no real gain in capacity was achieved. One possible way to achieve higher capacities is to design materials in which the metal–redox oxidation state can change reversibly by two units ($\text{M}^{n+2}/\text{M}^n$), while preserving the framework structure, and having molecular masses similar to those of the presently used 3d metal-layered oxides (for example, LiCoO_2). Such an approach is feasible with W-, Mo- or Nb-based metal oxides³⁷, but there is no overall gain in specific energy with these heavier elements. Inserting more than one Li ion per transition metal is also feasible with a few V-based oxides (V^{5+} is reduced to an average state of 3.5 in ' ω - $\text{Li}_3\text{V}_2\text{O}_5$ ' (ref. 38) or to 3.67 in $\text{Li}_5\text{V}_3\text{O}_8$). In principle, except for coordination number requirements, there is no obvious reason why this should not happen with other early transition metals and, in this respect, the recent finding of the reversible $\text{Cr}^{6+}/\text{Cr}^{3+}$ redox couple in a 3d metal-layered compound provides encouragement.

Tuning the morphology or texture of the electrode material to obtain porous and high-surface-area composite electrodes constitutes another exciting, although less exploited, route to enhance electrode capacities³⁹. Indeed, V_2O_5 aerogels, which are

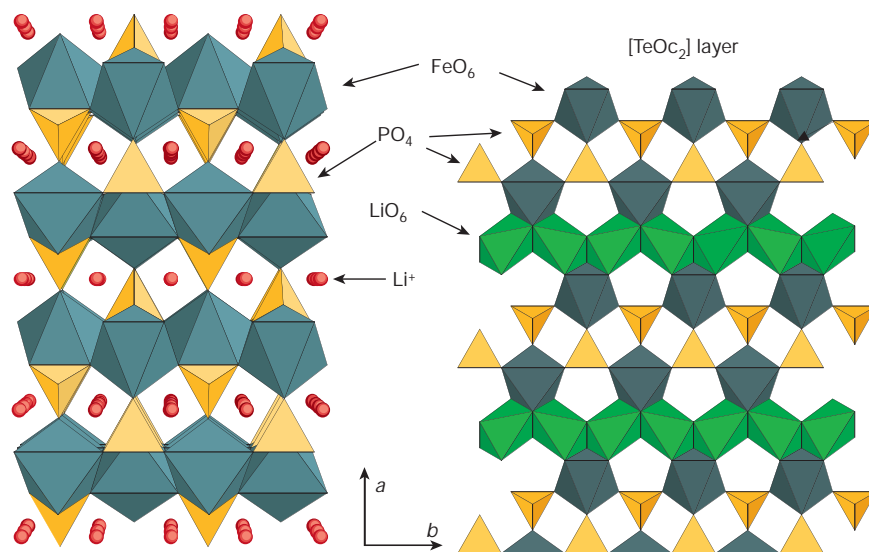


Figure 6 The crystal structure of olivine LiFePO_4 in projection along $[001]$. On the left, expanded view of the framework built on FeO_6 octahedra and PO_4 tetrahedra, with Li ions in red. The FeO_6 octahedra are linked together through corner sharing in the

(b , c) plane. On the right, restricted view of Li, Fe and P distribution between two distorted, h.c.p. (hexagonal close packed) oxygen-dense layers ($\text{P}_{10}[\text{LiFe}]_{\text{oct}}\text{O}_4$). LiO_6 octahedra share edges and Li ions may diffuse along $[010]$ and $[001]$.

mesoporous materials in which nanometre-sized domains are networked through a continuous, highly porous volume of free space, were reported recently to have electroactive capacities up to 100% greater than polycrystalline non-porous V_2O_5 powders and superior power rate capabilities⁴⁰ compared to usual V_2O_5 powders. Such extra capacity apparently derives from the onset of a pure capacitance, associated with the large surface area and high-porosity aerogel matrix, which adds to the existing faradic component. Conductive oxide aerogels such as V_2O_5 and MnO_2 therefore have the potential to boost the field of energy storage once the capacity penalty (in terms of Wh l^{-1}) attributable to their poor tap density ($\approx 0.2 \text{ g cm}^{-3}$) is over-

come. Tailor-made nanostructured materials, such as aerogels, create new opportunities not only at the applied level, but also at the fundamental level where some elementary questions, such as the exact mechanism governing these large capacities, remain unanswered.

A radically different approach⁴¹ takes advantage of the facile and reversible redox cleavage of the sulphur–sulphur bond to give lithium thiolate: $-\text{SS}- + 2\text{Li}^+ + 2\text{e}^- \rightleftharpoons -\text{SLi} + \text{LiS}-$. Depending on the electron, the voltage withdrawing power of the moieties attached to the sulphur can be up to 3 V (sulphur itself works at 2.4 V). Although promising in principle in terms of capacity and cost, these systems presently suffer from the relative low density of the reactants and solubility of the resulting thiolates in the electrolyte, leading to self discharge.

Materials for negative electrodes

As a result of numerous chemical (pyrolytic processing) or physical (mechanical milling) modifications, carbon negative electrodes⁴² display electrochemical performances that are improving continuously. Reversible capacities of around 450 mA h g^{-1} are now being reached, compared with a practical value of 350 mA h g^{-1} for graphite (372 mA h g^{-1} for the end compound LiC_6). In parallel, ongoing research efforts are focused on searching for carbon alternatives in the hope of finding materials (Fig. 4) with both larger capacities and slightly more positive intercalation voltages compared to Li/Li^+ , so as to minimize any risks of high-surface-area Li plating at the end of fast recharge, which are associated with safety problems. Such an effort resulted in the emergence of Li transition-metal nitrides as a new potential class of anode materials⁴³, owing to the large, stable and reversible capacity (600 mA h g^{-1}) displayed by one family member, $\text{Li}_{3-x}\text{Co}_x\text{N}$. This result triggered worldwide interest, although performances of the other newly reported Li-based nitrides unfortunately display inferior electrochemical performances compared to the Co phase. Furthermore, use of $\text{Li}_{3-x}\text{Co}_x\text{N}$ is constrained by the restrictive manufacturing requirements for handling such moisture-sensitive negative electrodes.

Throughout the search for carbon alternatives, much effort has been devoted to the use of Li alloys. The first commercial cell was

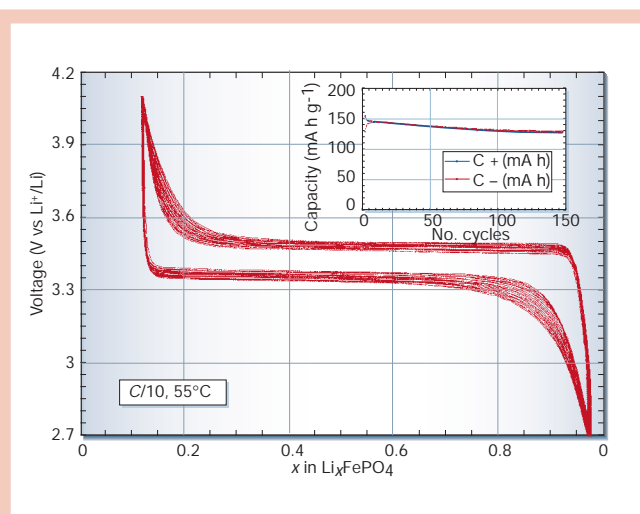


Figure 7 Cycling behaviour at 55°C of an optimized LiFePO_4/C composite electrode (83% of active material) at a scan rate of $C/10$. Fine particles of LiFePO_4 were obtained from annealing at 500°C a solid intimate mixture resulting from evaporation of an aqueous solution containing Li, Fe(III) and P precursors. The composite electrode was obtained from ball-milling LiFePO_4 with carbon SP. From ref. 36.

introduced in the 1980s by Matsushita; this was based on Wood's metal (a low-melting alloy of Bi, Pb, Sn and Cd), whose cycling performances were found to deteriorate with increased depth of discharge. While attractive in terms of gravimetric capacity, Li alloys suffer from cyclability issues resulting from large Li-driven volume swings (up to 200%), which cause disintegration and hence a loss of electrical contacts between particles. Although a reduction in alloy particle size clearly benefits the cyclability by increasing tolerance to stress cracking, so far the gains are not sufficient⁴⁴. However, it became clear that any physical or chemical means of overcoming the problem of reactant expansion should be beneficial, hence the use of composite negative electrodes. The basis behind this concept is the use of a 'buffer matrix' to compensate for the expansion of the reactants, so preserving the electrical pathway⁴⁵. Initially, such a buffer action was achieved by mixing two alloys that reacted at different potentials so that the electrochemically active phase was imbedded in a non-electrochemically active matrix.

A similar approach held considerable promise in 1997, when Fuji announced the commercialization of a new Li-ion technology (STALION) using an amorphous tin composite oxide (ATCO) as negative electrode. This reacts reversibly with Li at about 0.5 V, and has a specific capacity twice that of graphite⁴⁶. *In situ* X-ray diffraction studies of the ATCO electrode led to the conclusion that the Li reactivity mechanism in these composites was based on oxide decomposition by Li through an initial irreversible process to form intimately mixed Li₂O and metallic Sn, followed by a Li alloying reaction to form nanodomains of Li₄Sn embedded within the Li₂O matrix⁴⁷. However, the STALION cell was never commercialized, in spite of its announcement at the end of 1998. This was most likely due to poor long-term cyclability, the huge and irreversible capacity loss during the first cycle, which was reported by many groups, and the necessity of finding a convenient source for the two initial Li ions needed for the SnO reduction process.

Besides ATCO, other investigations, such as those pursued by Dahn *et al.*⁴⁸ on the -Sn-Fe-C system, have also revealed an appealing low-voltage reversible reactivity in composite materials developed as negative electrodes (in spite of initial irreversibility and short-lived capacities). The best experimental proof of the beneficial aspect of the buffer matrix arises from the ability to obtain several hundred cycles on a composite made by precipitating Sn metal at the grain boundaries of electrochemically inactive SnFe₃C grains⁴⁹. However, the cycling performance was improved at the expense of the electrode electrochemical capacity.

A new approach to alleviate the problems of alloy expansion, proposed by Thackeray *et al.*⁵⁰, involved selecting intermetallic alloys such as Cu₆Sn₅, InSb and Cu₂Sb that show a strong structural relationship to their lithiated products, Li₂CuSn and Li₃Sb for the Sn and Sb compounds, respectively. InSb and Cu₂Sb electrodes are particularly attractive candidates because they operate through a reversible process of lithium insertion and metal extrusion, with an invariant face-centred-cubic Sb array (that is, this array provides a stable host framework for both the incoming and extruded metal atoms). In the ternary Li_xIn_{1-y}Sb system (0 < x < 3, 0 < y < 1), the Sb array expands and contracts isotropically by only 4%, whereas the overall expansion of the electrode is 46% if the extruded In is taken into account. This expansion is considerably more favourable than the expansion of binary systems such as LiAl, which expand by ~200% during the phase transition of Al to LiAl. InSb and Cu₂Sb electrodes provide reversible capacities between 250 and 300 mA h g⁻¹. Despite the new and elegant concept behind the design of these intermetallic electrodes, they still suffer from poor cyclability, particularly upon the initial cycle; nevertheless, the approach deserves further study.

Based on the peculiar behaviour (that is, large capacity at low potential) of the transition-metal vanadates M-V-O, first proposed by Fuji Co.⁵¹ and later studied by several groups, Poizot *et al.*⁵² reinvestigated the reactivity of Li-metal oxide. Surprisingly, they found a Li electrochemical activity for well known oxides, but these

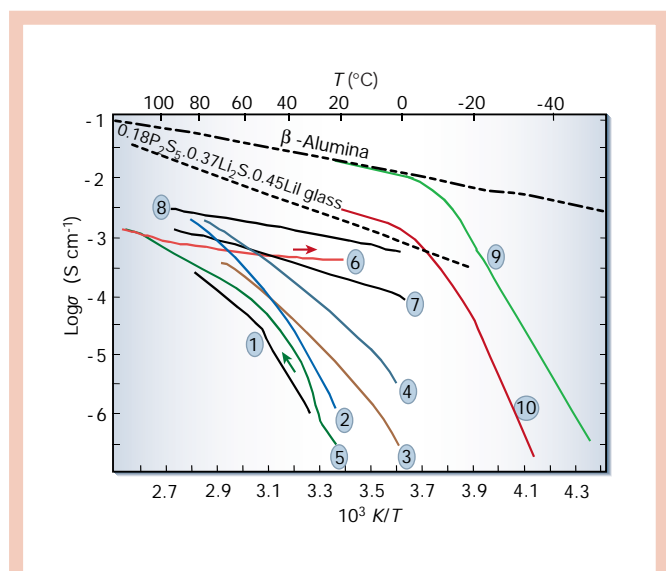


Figure 8 Arrhenius plot of conductivity for various solid electrolytes. 1, First-generation PEO-LiCF₃SO₃; 2, new solutes with high-dissociation PEO-Li[(CF₃SO₂)₂N]; 3, low-*T*_g combination polymer; 4, plasticized polymer electrolyte PEO-Li[(CF₃SO₂)₂N] + 25% w/w PEG-dimethylether (molecular weight, 250); liquid crystalline polymer electrolytes; 5, heating curves; 6, cooling curve⁶⁴; 7, gel-type polymer (X-linked PEO-dimethacrylate-Li[(CF₃SO₂)₂N]-PC 70%); 8, liquid electrolyte PC/DME LiCF₃SO₃; 9, liquid electrolyte EC/DMC-LiPF₆ at low temperature⁶¹; 10, gel electrolyte P(VDF-HFP)/EC/DMC-LiPF₆ (ref. 61).

did not react with Li according to the classical processes of Li insertion–deinsertion or Li alloying, the catchwords of the past 20 years. For instance, MO-type compounds (where M is Co, Ni, Fe, Cu or Mn), having a rocksalt structure and containing metal elements (M) that do not alloy with Li, exhibited capacities two to three times those of carbon with 100% capacity retention for up to 100 cycles. The mechanism of Li reactivity in such materials differs from the classical processes, and is nested in the electrochemically driven, *in situ* formation of metal nanoparticles during the first discharge, which enables the formation and decomposition of Li₂O upon subsequent cycling⁵³. Remaining issues relate to a problem of surface, with the chemical reactivity being enhanced as the particle size becomes smaller. These findings open new avenues of research aimed at capitalizing on the beneficial effect that particle-size confinement could have within the field of electrochemistry. These and related nanocluster systems under development hold much promise for future developments.

Polymer and liquid electrolytes

Besides the electrodes, the electrolyte, which commonly refers to a solution comprising the salts and solvents, constitutes the third key component of a battery. Although the role of electrolyte is often considered trivial, its choice is actually crucial, and is based on criteria that differ depending on whether we are dealing with polymer or liquid-based Li-ion rechargeable batteries⁵⁴. For instance, working with a highly oxidizing (>4V versus Li/Li⁺) positive electrode material for Li-ion batteries requires electrolyte combinations that operate well outside their window of thermodynamic stability (3.5 V). This is the reason why early workers in the field ignored very positive cathode materials. But fortunately this electrolyte stability is kinetically controlled, enabling the use of non-aqueous electrolytes at potentials as high as 5.5 V (ref. 55). Similarly, the use of a polymer rather than a liquid electrolyte adds further selection criteria linked to the electrochemical stability of the polymer⁵⁶. There are numerous liquid solvents available, each with different dielectric constants and viscosity, and we can select specific solvents to favour the ionic

conductivity of the electrolyte. In contrast, there are only a few Li-based salts or polymers to choose from, the most commonly used ones being based on polyethylene oxide (PEO). The results from research efforts aimed at counterbalancing this deficit have led to the present level of research and development on electrolytes.

Guided by general concepts of viscosity and dielectric constants, optimizing the ionic conductivity of a liquid electrolyte almost becomes a field-trial approach with the hope of finding the key ingredients. For instance, only ethylene carbonate can provide the *ad hoc* protective layer on the surface of graphite that prevents further reaction (continuous electrolyte reduction and self-discharge). Ethylene carbonate is therefore present in almost all commercial compositions, thinned with other solvents owing to its high melting point. Why the homologous propylene carbonate is unsuitable for this protective layer remains an open question, reminding us that chemistry has its secrets.

In contrast, achieving high ionic conductivity in Li-based polymer electrolytes requires a better understanding of the fundamentals of ion dissociation and transport. Both the nature of the polymer–salt interaction and the precise structure of highly concentrated electrolyte solutions have always resisted rationalization. Nevertheless, a principal goal has been to search for new, highly conductive salts with a large electrochemical window, which form a eutectic composition with PEO that melts at the lowest possible temperature⁵⁷. The concept of non-coordinating anions with extensive charge delocalization was achieved with the perfluorosulphonimide $\text{Li}^+[\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_3]^-$ salt (abbreviated as LiTFSI)⁵⁸. Figure 8 shows the marked improvement when passing, with simple PEO, from a ‘conventional’ LiCF_3SO_3 salt (curve 1) to the imide salt (curve 2), where an order of magnitude is gained, not ignoring the larger elastomeric domain towards low temperature. The polymer architecture has a role independently of dissociation. Attaching the side chains of the solvating group to the polymer increases the degrees of freedom as a result of dangling chain ends; this improves conductivity (Fig. 8, curve 3), but compromises the mechanical properties.

Although efforts aimed at enhancing the ionic conductivity of polymer electrolytes have been insufficient to permit operation at room temperature, they have benefited liquid-based electrolyte systems in terms of cost and safety, so that battery manufacturers of Li-ion cells are eager to see the further development of organic anion-based salts able to operate at voltages greater than 4.5 V. LiTFSI is an example of this cross-fertilization. Although extremely resistant to oxidation itself, the electrochemical use of such a salt is limited to 4 V in presence of an Al collector, because a stable and soluble Al salt can be formed as a consequence of the robustness of the anion bonds. With the less stable coordination anions (LiPF_6), decomposition occurs immediately and is accompanied by formation of protective AlF_3 . However, owing to its high conductivity in any medium, its safety and lack of toxicity, LiTFSI is being used increasingly in Li-ion batteries, the corrosion problem having been solved by simple addition of a passivating coordination-type salt. A wide range of anion-forming systems now exists, especially in the imide family, and these are viewed as candidates for high conductivity and Al passivation.

Having exploited most of the possibilities offered by ‘dry’ polymers to improve conductivity (ability, amorphous state and lowest possible glass-transition temperature T_g controlling the ion mobility), a remaining option was to use additives, known in polymer science as plasticizers, to act as chain lubricants, so leading to the development of ‘hybrid’ polymer electrolytes⁵⁹. Indeed, suitable plasticizers are chosen between the same polar solvents as for liquid electrolytes⁶⁰, such as propylene carbonate, γ -butyrolactone or polyethylene glycol ethers, or are formed from short-chain PEO (4–25 monomer units). A lightly plasticized material (10–25% additive) improves conductivity by an order of magnitude (Fig. 8, curve 4). Gels, on the other hand, contain 60–95% liquid electrolyte, and are only 2–5 times less conductive than their liquid counterpart⁶¹

(Fig. 8, curves 7–10). Interestingly, when the gelling agent is a polyether, most of the solvation still takes place through the polymer chains rather than the carbonate solvents, the latter being less prone to donate electron pairs. Understandably, the lightly plasticized systems can be used in a Li-metal configuration, as much of the resilience of the pristine polymer is retained, whereas the much softer gels require a Li-ion configuration.

It is surprising that in spite of the direct link between their ionic conductivity and their degree of amorphicity, very little is known about the structural chemistry of polymer electrolytes. In contrast to the well established dynamic view of ionic conductivity on these materials, Bruce *et al.*⁶² recently proposed a structural view, highlighting the importance of aligning or organizing the polymer chains in order to enhance the levels of ionic conductivity. Similarly, Wright and co-workers⁶³ and Ingram⁶⁴ focused on the liquid crystalline state to force the solvating polymer into a conformation that was dictated by the liquid crystal part. The result is a partial decoupling of the conductivity from the glass-transition temperature of the polymer. The conductivity of such liquid crystalline chain polymers is low at room temperature, but reaches liquid-like values at high temperature or when kept under polarization, and remains so upon cooling to room temperature (Fig. 8, curves 5 and 6), without appreciable activation energy⁶⁴. As these new perspectives generate renewed interest in the design of polymer electrolytes, it is hoped that solutions may eventually be found to the problems of ionic conductivity afflicting this class of materials at ambient or subambient temperature.

The addition of nanoparticle fillers (10% w/w), such as Al_2O_3 or TiO_2 , to simple PEO compounds increases the conductivity several-fold at 60–80 °C, and prevents crystallization for at least several weeks at room temperature⁶⁵. Two important advantages of these systems are an increase in the apparent Li transport number, from a low of ≈ 0.3 (common to polymer, liquid and gels) to ≈ 0.6 , and the formation of a stable, low-resistance interface in contact with Li. Because these materials obey different conduction mechanisms, they are presently the focus of many studies, both practical and theoretical⁶⁶.

Technologies based on either solid polymer or ‘hybrid’ polymer electrolytes offer great advantages that will be necessary to meet the flexible, shape-effective requirements dictated by today’s electronic miniaturization, while at the same time providing a larger autonomy. Current Li technologies rely on liquid-jellyroll or prismatic-cell configurations. Neither fits well in a multiple-cell configuration. This is in marked contrast with the recent thin, plate-like plastic (PLiON) technology that enables excellent packing efficiency, as multiple plates can be densely packaged in parallel within one cell while preserving the flexibility of the overall package. Future technology improvements should focus on better chemical engineering of the bonded laminates, so as to obtain even thinner cells. Similar attributes can be provided by the solid Li–polymer technology, which in addition exhibits extra capacity and is free of electrolyte leakage. This currently operates at 80 °C. Although warm temperatures may be an advantage for the large batteries required by the transportation sector, problems of conductivity have to be solved for electronic applications, as emphasized earlier.

The electrode–electrolyte interface

The Li-ion cell density can be improved through a selective use of appropriate existing or new materials for negative and positive electrodes. However, optimizing an electrode material is only the first step in the process leading to its implementation in a practical cell. Indeed, while the capacity of a cell is nested in the structural or electronic behaviour of its electrode, poor cell lifetimes are rooted mainly in side reactions occurring at the electrode–electrolyte interface. Thus, mastering the chemical stability of any new electrode material with respect to its operating liquid or polymer electrolyte medium, which requires a control of the electrode–electrolyte interface through surface chemistry, is as important as designing new

materials. Tackling interfacial issues is both tedious and complex. We should remember that, despite many years of research devoted to the mechanism by which the solid electrolyte interphase forms on Li or carbonaceous materials, its composition and nature are still the subject of much controversy. In contrast, the positive electrode interface has received little attention over the years, despite its equally crucial role. Its importance is amplified with the Li-ion technology, where high voltages exceed the electrochemical resistance of the electrolyte oxidation, and even favour its catalytically driven decomposition. Thus, it is critical to control the electrode surface so as to modify its catalytic activity towards electrolyte decomposition. The strategy developed to address this issue uses coatings that encapsulate, through chemical or physical means, the electrode grains with either an inorganic or an organic phase. This concept, successfully applied to the spinel LiMn_2O_4 , is based on minimizing the surface area of the active material in direct contact with the electrolyte³³. The coating must allow easy diffusion of Li ions and, although insulating in nature, must be thin enough to allow the electrons to tunnel through. Equally relevant is the unexplained role of filler additives in polymer electrolytes⁶⁵, which markedly reduce the interfacial impedance in contact with Li.

Thirty years after its initial observation, the key issue of Li dendrite growth, which was thought to be governed mainly by current densities, remains highly topical, especially in light of recent promising results obtained by Aurbarch's and Bates' groups. Revisiting Exxon's solvent 1-3-dioxolane, Aurbarch and co-workers⁶⁷ showed that the use of LiAsF_6 salt led to a completely different Li morphology from that obtained from an ethylene carbonate–dimethyl carbonate (EC–DMC) electrolyte. They explained this in terms of the reactivity of dioxolane with lithium, which forms an elastomeric coating endowing the Li surface with plasticity and flexibility, thereby reducing dendrite growth. These findings were implemented in Li/MnO₂ commercial Tadiran cells that, under well defined cycling conditions, are claimed to be safe. The bulk polymerization of the cyclic ether, initiated at the positive electrode on overcharge, acts as a thermal shutdown. Even more spectacular are recent reports by Bates *et al.*⁶⁸ who succeeded in cycling LiCoO_2/Li thin-film batteries for more than 50,000 cycles using a glassy electrolyte in $\approx 1\text{-}\mu\text{m}$ -thick films obtained by sputtering techniques. By controlling the uniform Li stripping–plating mechanism, the same authors demonstrated the feasibility of a Li-free, rechargeable, thin-film battery — that is, cells constructed in the discharged state with no Li metal initially present⁶⁹. Such findings, whether resulting from low-current density or the use of solid electrolyte, show that the problem of dendrite growth can be solved, at least with special cell configurations. Visco and co-workers⁷⁰ recently showed that a glassy nanometric layer deposited on Li metal completely insulates it from its environment, even in the presence of liquids, and that this coating can be applied at a high production rate. With further work devoted to the implementation of these findings to large-size Li batteries, the development of a Li-free rechargeable battery remains a realistic goal for the future.

The principal challenge for Li-based rechargeable batteries, or indeed for any battery, lies in gaining better understanding and control of the electrode–electrolyte interface in the hope of designing new solid–solid or solid–liquid interfaces. For example, the nature of the secondary reactions occurring at high temperature, which cause cell failure, remains an unanswered question that must be addressed to ensure the practical success of these technologies. In this case, however, the main difficulty stems from a lack of available techniques to probe the evolution of the electrode–electrolyte interface at a local level. We have so far relied (with the exception of X-ray diffraction) on post-mortem rather than *in situ* studies to determine how the electrodes or interfaces age with time either under cycling or storage conditions, thereby missing key information. But introduction of the plastic Li-ion-type technology has created new opportunities to perform a wide variety of *in situ* characterization techniques. These include X-ray absorption near-edge structure, nuclear magnetic

resonance and Mössbauer spectroscopies, or even scanning electron microscopy observations that allow real-time visualization of dendrite growth at an interface⁷¹. Efforts aimed at developing new characterization tools must be vigorously pursued so as to create a comprehensive database on the electrode–electrolyte interface.

Conclusion

Consumers are in constant demand for thinner, lighter, space-effective and shape-flexible batteries with larger autonomy. Such demand will continue to generate much research activity towards the development of new cell configurations and new chemistries. In this review we hope to have conveyed the message that the field of energy storage is advancing faster than it perhaps has ever done in the past. The benefits, in terms of weight, size and design flexibility provided by today's state-of-the-art Li-ion configurations, which owe much to the design engineers' striving to develop efficient, economical microtechnologies, are a good illustration. The Li-based battery chemistry is relatively young, and as such is a source of aspirations as well as numerous exciting challenges. The latter are not limited to solid-state chemists. The effort should be highly multidisciplinary with strong roots in the fields of organic and inorganic chemistry, physics, surface science and corrosion. Through materials design we can expect significant improvements in energy density. And although designing new materials can be intuitive or based on chemical concepts, coupling these efforts with those of theorists who are able to perform band-structure calculations on envisioned compounds will prove to be highly beneficial. Of equal importance is a better understanding of the electrode–electrolyte interface to facilitate design of new interfaces. Here the goal is well defined, although we must diverge from the empirical approach used so far, and make full use of the recent progress achieved by *in situ* characterization. As Li-rechargeable batteries enter their teenage years, scientists and engineers predict an even brighter future lies ahead. □

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