

Materials for next-generation lithium batteries

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Likely developments awaiting the science and technology of next-generation lithium batteries form the focus of this article. New anode materials based on nano-structured carbons and lithium-alloying metals, novel eco-friendly cathode materials, safe and non-flammable aprotic electrolytes, and polymer electrolytes are discussed. Possible scenarios for improvements in existing or presumed battery active materials are suggested. Advances in the science and technology of lithium batteries are previewed with a prognosis of challenges and opportunities in the development of marketable materials and products.

Keywords: Battery safety, ionic liquids, lithium batteries, nanomaterials, organic radical battery.

A BATTERY is an electrochemical device that converts the chemical energy stored in its active materials directly into electrical energy by means of an electrochemical oxidation–reduction (redox) reaction. Beginning with the discovery of the lead–acid battery by Gaston Planté in 1859, we have seen substantial progress in battery chemistries to cope with the ever-increasing power demands of newly emerging devices. Indeed, gone are the days when batteries had only limited applications, as in flashlights, valve radios, starting–lighting and ignition in vehicles, emergency lighting and telephony. In fact, it is impossible to think of a world without batteries, for they are so ubiquitous. From home (flashlights, radios, clocks, door chimes, lawnmowers), consumer and entertainment (wristwatches, children’s toys, DVD players, MP3 players, digital cameras), communication (landline and cellphones, PDAs, computers), transportation (SLI, central locking system, power windows), industry (forklift trucks, power tools), medicine (hearing aids, heart pacemakers), military (sonobuoys, missiles, ships, submarines) to aerospace (aircraft, satellites, space stations), batteries are everywhere. Today, original equipment manufacturers demand made-to-size power packs that can fit into their battery compartments. In keeping with the demands, the last few decades have witnessed tremendous changes in battery design, shape, size and capacity, from pin-type and wafer-thin cells of a few milliampere hours as for fishing nets and credit cards to large banks of several thousand ampere hours as for load levelling.

Viewed against the backdrop of a burgeoning portable electronics and consumer industry that continually demands smaller, thinner and lighter power packs, lithium batteries are poised for a niche market with an attendant shift of gears in technology. The world market for lithium secondary batteries exceeded US\$ 5 billion in 2005 and is projected¹ to reach US\$ 10 billion by 2009. This calls for a parallel development in materials engineering and processing not only to achieve improvements in materials that are in current use, but also to develop novel materials with higher performance for a next generation of batteries. This article focuses on efforts towards this goal and developments in related areas.

Need for new-generation batteries

A look at today’s battery-application scenario shows that the workhorse for automobile starting–lighting–ignition is still the lead–acid battery with the nickel–cadmium and nickel–metal hydride systems as the mainstays for aerospace and military equipment, and lithium-ion batteries as the choice for portable electronic devices. There was some noise on the rechargeable alkaline manganese-dioxide chemistry making inroads into the world market, but the take-off has only been muted. On the contrary, development of lithium-ion batteries, based on intercalation electrodes (Figure 1), has emerged as the most noticeable achievement of modern theoretical and applied electrochemistry. At present, lithium-ion batteries are the canonical rechargeable power sources compatible with portable electronics, and have energy densities in excess of 190 Wh/kg. It must be noted that not much changes have

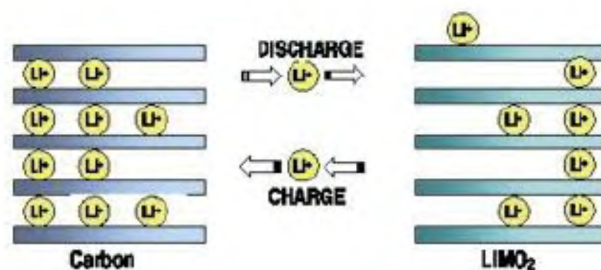


Figure 1. Working principle of lithium-ion batteries. The anode is graphite and cathode is a layered lithiated transition metal oxide. The operation involves a cyclic transfer of lithium ions between the electrodes.

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been made in the technology of lithium-ion batteries since their commercial introduction by Sony in 1990. The limited advances that have been made include: (i) replacement of 70–80% of the Co in LiCoO_2 with Ni, a move that substantially increases the capacity and improves overcharge stability; (ii) developments in other cathodes, such as LiMn_2O_4 and LiFePO_4 , offering cost and safety advantages over LiCoO_2 , and (iii) stabler and non-flammable electrolytes, including polymer electrolytes.

It is clear that lithium battery technology will soon be found wanting with new applications unveiled by the day. It is now acknowledged that lithium battery technology has not kept pace with the rapid miniaturization in electronic circuitry, which requires high-energy batteries for specialty applications as, for example, on-board power. There are also other applications such as telecommunication satellites that thirst for power, where the current lithium battery technology falls short. The ambit of lithium batteries is bound to grow beyond hand-held devices with their projected use in electric and hybrid vehicles. They also find use in large stationary power units, an example being Avestor's lithium metal polymer batteries for telecommunication back-up².

The use of lithium batteries for such applications as electric vehicles presents formidable obstacles, both economic (cost of new technologies) and engineering (thermal management). Moreover, battery performance must be in tune with the application, which means playing with different cell chemistries to meet specifications. Despite a plethora of safety standards that lithium batteries pass through, safety remains a major concern. The recent massive recall of 4.1 million lithium-ion batteries in their laptops by Dell is just among the several that have happened in the short history of lithium-ion battery technology³. Indeed, in addition to their capacity restraints, the low-tolerance technology of present-day lithium-ion batteries is a major deterrent in their market drive. The low tolerance is a direct fallout of the inherent chemistry of the system that combines highly reactive substances in contact with combustible electrolytes in a restricted volume.

Safety hazards are all the more of concern if the power packs are large, limiting applicability in thrust areas such as electric traction. It must be noted that for multi-cell configurations, additional protection devices must be incorporated, which can raise the cost of the battery and lower its performance. If the active circuits consume power, albeit being low, they eat into the capacity and life of the battery. Cost is often a constraint in the large-scale applicability of lithium batteries, especially for low-cost gadgets. It must be noted that nearly 90% of the material cost of lithium-ion batteries goes into the overcharge/over-discharge protection mechanism, active materials (mostly for the cobalt-based oxide cathode), electrolytes (especially for salts such as LiPF_6), and the microporous multi-layer separator. Continual reports appear in the literature on new materials with high performance and on

improvements in existing materials. A majority of these reports relate to novel nanostructures, reflecting current trends in materials research. Thus, there is ample scope for moving towards lithium-ion batteries that are safer, less expensive, non-toxic, and constructed with materials that outperform present-day active and passive components. In this vein, this article will discuss emerging trends in anode and cathode active materials (especially as nanoscopic structures), electrolytes (polymer electrolytes, non-flammable liquid electrolytes, and ionic liquids), and safety-related aspects.

Active materials

Anode materials

The most common among anode materials are carbon and lithium-alloying metals. The host element in the graphite intercalation compound/alloy 'shields' the inserted lithium, making the alloy less reactive towards electrolytes. As a result, the chemical potential of lithium in the lithiated material is less than that in metallic lithium. This translates into a safety advantage, which, however, comes with a penalty in cell voltage and, therefore, also in energy and power density. Besides, the charge-discharge performance of these alternative anode materials also depends on the rate of diffusion of lithium in the host matrix. A limiting factor in the applicability of these materials is the volume change that accompanies the charge-discharge processes. The resulting mechanical stress associated with the large volume changes in the case of alloys, for example, 96.8% for Li–Al alloy⁴, limits their applicability compared to graphite⁵ that increases by only 9.4% in volume upon lithiation to LiC_6 .

Carbonaceous anodes: With its cost, availability and electrochemical properties favourable, carbon is a prime anode material in lithium-ion batteries. The theoretical lithium-intercalation capacity of graphitic carbon is a poor 372 mAh/g (for a stoichiometry of LiC_6) compared to 3862 mAh/g, the charge density of lithium. The chemical diffusion coefficient for lithium in carbon⁶ is of the order of 10^{-9} sq. cm/s. Graphitic carbons are currently at the centre stage of anode materials in commercial lithium-ion cells. However, amorphous carbons are also gaining importance as potential anodes for they possess several desirable features such as: (i) higher uptake of lithium, often much higher than the theoretical limit of 372 mAh/g that only perfectly graphitic structures can offer⁷, (ii) their amenability to doctoring by varying the nature of their organic precursors and temperature protocols, and (iii) good cycling ability. Disordered carbons obtained by pyrolysis of organic precursors contain a predominantly planar hexagonal network of carbons, but lack extended crystallographic ordering. The high insertion capacities of pyrolytic carbons have been associated with both disorder

and hydrogen content. Although several models have been proposed to account for the additional capacity exhibited by disordered carbons, our understanding of the relationship between the structure and reversible lithium insertion properties of disordered carbons remains limited by the absence of long-range order in these carbons.

The energy density of lithium-ion batteries based on carbon has been increasing by about 10% annually. This has been facilitated largely by successive improvements in the charge–discharge efficiency and discharge capacity of carbonaceous anodes by a combination of structural and surface modifications. However, to combat the onslaught from competing anode materials, further improvements are required. Hitachi Chemical Company, Japan has developed an artificial graphite by optimizing the particles and the pore structure⁸. This graphite exhibits a practical specific capacity of 360 mAh/g with 95% charge–discharge efficiency and can sustain high discharge rates.

Novel graphite varieties: Most synthetic approaches to graphitic anodes require heat treatment at temperatures around 3000°C, which makes processing energy-intensive and often calls for management of evolving gaseous products. Much effort is now being expended on using modified natural graphites and other graphitic carbons such as kish graphites^{9,10}. Recent studies on modified graphites show that air oxidation of natural graphites results in products with improved electrochemical characteristics^{11,12}. Replacement of natural graphites with kish graphites (Figure 2) should be of immediate interest as kish graphites exhibit lithium intercalation capacities well above the theoretical value of 372 mAh/g that can be tapped from perfectly graphitic structures^{9,10}; kish graphite production is rather inexpensive and involves relatively low temperatures of around 1500°C.

Carbon nanotubes: Much interest has been evinced in the use of carbon nanotubes (CNTs) as anodes in lithium-ion batteries. Multi-walled carbon nanotubes (MWCNTs) are particularly attractive as high-capacity anodes for lithium storage. They provide a variety of lithium accommodation sites, namely, spacing between the graphite layers, local turbostratic disorders arising from their highly defective structures, and the central core. In fact, studies^{12,13} have shown lithium intake of more than 1400 mAh/g in CNTs. Their irreversible capacities, however, are too large to merit practical applicability. For improving the capacity of CNT-based anodes, their composites with lithium-alloying metals have been investigated. However, such composites exhibit capacities between those of the CNTs and the alloying metal. Investigations on CNT–metal combinations include those with Sn (ref. 14), Sn₂Sb (ref. 15), SnNi (ref. 14) and AgFeSn (ref. 16). Recently, Kumar *et al.*¹⁷ demonstrated metal-filled CNTs as novel high-capacity lithium-insertion anodes. For example, Sn-filled MWCNTs exhibit capacities much higher than the

cumulative values that can be expected from the constituents, with first-cycle deinsertion capacities of as high as 889 mAh/g (Figure 3)¹⁷. Filling with other metals has also yielded high reversible capacities. But the irreversible capacities of metal-filled CNTs and their high cost are deterrents to their commercial exploitation. CNTs have good chemical stability, and possess high tensile strength (~50 GPa) and shear strength (~500 MPa); these properties hold promise in improving the longevity of the anode. The short diffusion distances for lithium ions that the host provides result in enhanced dynamics of the charge-transfer processes, facilitating high charge–discharge rates. CNTs also have high electrical conductivity (10^{-4} S/cm) and thermal conductivity (2000–4000 W/mK), which enable high power output from the electrodes employing them. Accordingly, CNT-based lithium-insertion anodes are expected to be high-strength, durable electrodes with much improved energy and power densities.

Exploitation of the special properties of aligned carbon nanotube (ACNT) arrays for highly ordered, high surface-

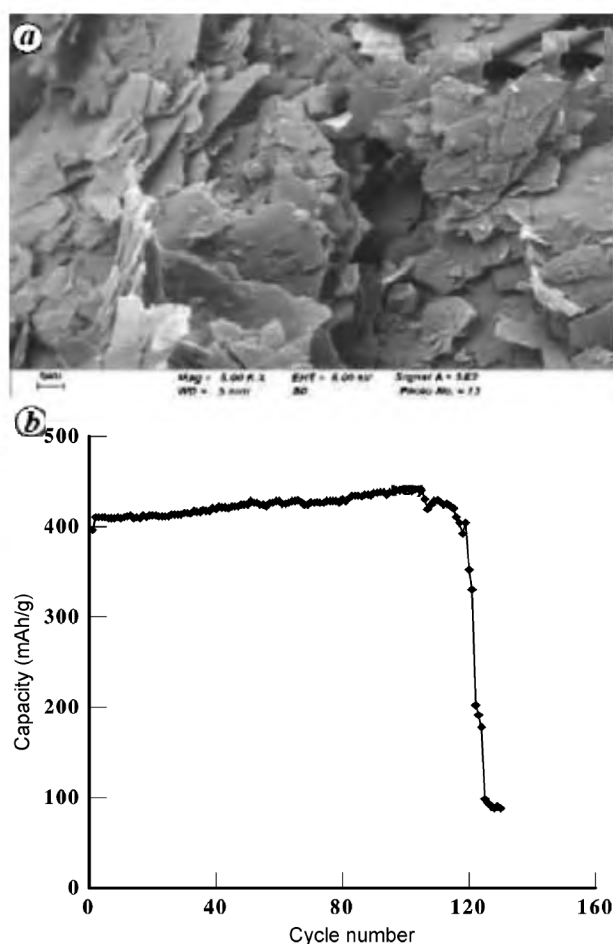


Figure 2. *a*, SEM image of kish graphite showing flaky surface morphology⁸. *b*, Cycling behaviour of kish graphite (3.000–0.005 V; 0.1 C rate).

area electrodes with excellent electronic and mechanical properties is possible only if methods are developed for making ACNT composites that are mechanically robust and sufficiently conducting in the horizontal direction. Removal of ACNTs from their substrates would damage any metal coating provided for conductivity. In a recent breakthrough, Chen *et al.*¹⁸ used a conducting polymer composite layer to bring about not only electrical connectivity, but also mechanical robustness. The composite layer is so thin that 90% of the CNT length is exposed, allowing their use in a variety of applications, including lithium-ion batteries.

Aligned MWCNTs produced by pyrolysis of iron(II) phthalocyanine¹⁹ on a quartz plate were given a 100-nm thick coating of poly(3,4-ethylenedioxythiophene) (PEDOT) by chemical vapour pyrolysis. The high electronic conductivity of PEDOT ensured good electrical connectivity of the individual nanotubes in the array. Mechanical stability was ensured by a second coating of 500 nm of poly(vinylidene fluoride) (PVDF). This resulted in a flexible CNT array electrode, which could be peeled-off the quartz substrate without damage. Indeed, the electrode could not be damaged even by rubbing or abrasion on a hard surface. The conductivity of the free-standing array electrode was over 200 S/cm, which was significantly higher than that of an ACNT/PVDF electrode without the conductive PEDOT layer (2–20 S/cm). Chen *et al.*¹⁸ also assembled a lithium-ion battery with this array anode. Although the electrode exhibited a rather high irreversible capacity (due to extensive SEI formation on its

high-area surface), it gave a stable discharge capacity of 265 mAh/g over 50 cycles. A significant improvement in the use of this electrode is that it renders the use of a copper current collector superfluous²⁰. The absence of copper substrate means that the weight of a typical CNT array electrode would be as small as 2 mg compared to 14 mg for one that uses a copper substrate¹⁸. Another advantage is the long-term stability of the electrode free from impurities released by copper dissolution in the electrolyte. The study provides a new strategy towards lightweight, flexible, highly conductive and mechanically robust rechargeable batteries.

Alloy anodes: Following the demonstration of metals being alloyed with lithium in aprotic solvents²¹ as early as in 1971, a large number of publications have concentrated on exploiting this discovery for lithium-ion battery applications. Li–Al alloys are among the first to be studied as anodes for lithium-ion batteries. Aluminum forms two alloy phases with lithium with different lithium, transport properties: α -Li–Al (Li^+ -diffusion coefficient: 10^{-12} sq. cm/s) and β -Li–Al (Li^+ -diffusion coefficient: $4\text{--}8 \times 10^{-10}$ sq. cm/s)²². The cyclability of this alloy can be enhanced by the addition of substances such as dilithium phthalocyanine, which modify surface films on the anode²³. However, a critical problem in the exploitation of Li–Al alloy anodes is volume change during the lithiation and delithiation processes. This problem was sought to be overcome by the use of ‘dimensionally-stable’ anodes. Specifically, this means the use of: (i) submicron particles of the alloy phase embedded in a ‘stabilizing matrix’, or (ii) an intermetallic host in which one metal alloys with lithium (e.g. Al, Bi, Cd, Mg, Pb, Sb, Sn, Zn), while the other does not (e.g. Co, Cu, Fe, Ni). Such an approach would result in a matrix with particles of suitable grain sizes that buffer any mechanical stress accompanying the alloying and dealloying processes. It is well recognized that the microstructure of the alloys has a definite influence on their performance as an anode. For example, a promising alloy anode composed of a eutectic mixture of Al and Al_3Ni has an inactive phase in Al_3Ni , which bestows mechanical stability to the anode, while the free aluminum participates in the electrochemical reactions²³. Sn–Cu intermetallics have also shown promise as alternative anode materials²⁴.

Battery scientists today are evincing renewed interest in alloys and intermetallic compounds that can replace graphitic carbon in lithium-ion batteries. These alloys also offer higher theoretical volumetric capacities than graphite; for example, InSb with a constant electrode density of 5.6 g/cubic cm yields 1904 mAh/cubic cm as against 818 mAh/cubic cm for graphite with a density of 2.2 g/cubic cm.

Among the most extensively studied intermetallic anodes are those based on tin, typical examples being Cu_6Sn_5 (ref. 25), FeSn_2 (ref. 26) and SnSb (ref. 27). Al-

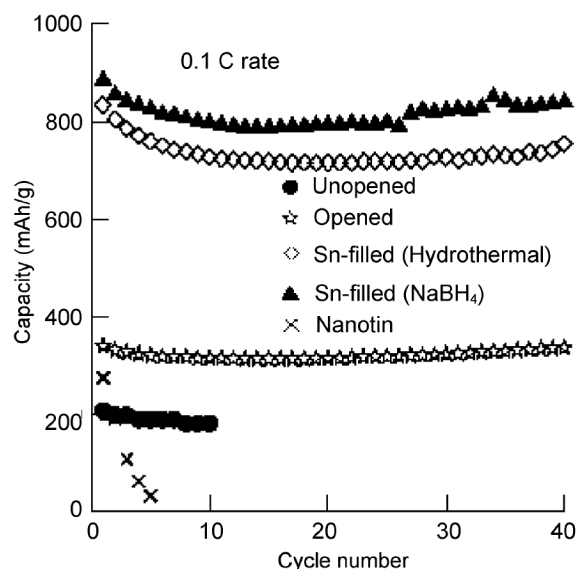


Figure 3. Comparison of the cycling behaviour of nanotin, the unopened, opened but unfilled, and tin-filled carbon nanotubes (0.000–3.000 V, 0.1 C rate). Tin filling was done by capillary filling of opened carbon nanotubes with a melt of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ followed by reduction by a hydrothermal method or by NaBH_4 (ref. 16).

though the capacity retention of intermetallics such as Ni_3Sn_4 is better than that of plain tin electrodes, they are unsuitable for prolonged cycling²⁸. It is now believed that the electrochemical behaviour of such electrodes can be improved by optimizing their morphology and intermetallic space. Hassoun *et al.*²⁹ obtained a stable capacity of 300 mAh/g over 70 cycles with electrodeposited Ni_3Sn_4 electrodes at 1C rate. However, the results are unsatisfactory given the higher performance levels expected of batteries for electric traction. Recently, high-performance Ni_3Sn_4 nanoarchitected anodes have been proposed³⁰ that deliver about 500 mAh/g without decay over 200 test cycles. The electrodes also give 20% of their theoretical capacity at rates as high as 10C (ref. 31). Antimony-based alloy anodes have also proved attractive, e.g. Ag_3Sb (ref. 31), CoSb_3 (ref. 32), $\text{Co}_{1-2y}\text{Fe}_y\text{Ni}_y\text{Sb}_3$ (ref. 33), CrSb_2 (ref. 34), Cu_2Sb (ref. 35), InSb (ref. 35), Mn_2Sb (ref. 36) and TiSb_2 (ref. 37). Although these intermetallics exhibit slightly lower capacities than pure antimony (660 mAh/g), their cycling behaviour is superior.

Silicon: This is a possible alternative to carbonaceous anodes as it has a capacity of 4199 mAh/g, corresponding to a composition of $\text{Si}_5\text{Li}_{22}$. It is also the second most abundant element on the earth's crust. However, the large capacity fade observed during initial cycling and volume changes of as much as 400% accompanying the charge-discharge processes³⁸ have prevented silicon anode from commercialization. Several methodologies have been adopted to reduce capacity fade, which include use of: (i) thin films of silicon, (ii) micro- and nano-scale silicon powder, (iii) dispersions of silicon in active and inactive matrices, and (iv) silicon with different binders. Much remains to be done to realize silicon-based anodes with optimal performance characteristics. Recently, Kwon *et al.*³⁹ reported a first-cycle insertion capacity of 1257 mAh/g with a significantly enhanced Coulombic efficiency of 71% for silicon quantum dots coated with amorphous carbon; these authors surmise that a uniform distribution of silicon nanoparticles in the carbon layer prohibits aggregation of the active particles during cycling³⁹. The cost of production of silicon quantum dots, however, remains a major impediment towards commercialization of such anodes.

Conversion electrodes: Lithium-ion cells are concentration cells in which lithium ions are cyclically transferred between two intercalation/insertion electrodes. Electroinsertion reactions are intrinsically simple and reversible. By conventional wisdom, in order to support electroinsertion reactions, electrode materials must be electronically conducting and must have crystallographic voids through which lithium ions can diffuse. However, several interstitial-free 3d-metal oxide structures, unsuitable for intercalation chemistry and hitherto been disregarded for rechargeable lithium battery applications, have been shown^{40,41}

to exhibit reversible capacities as large as 1000 mAh/g. This has led to investigations into conversion reactions involving nitrides, fluorides, phosphides, sulphides and borides, and reactions with as many as four electrons per 3d metal have been reported⁴¹. The staggeringly high capacities are realized with low-cost metals such as iron and manganese. It is noteworthy that the appeal of conversion reactions lies in the nanostructured character of the active material, which is internally created. However, their applicability is limited by the large hystereses in their charge-discharge curves⁴². At any rate, it is obvious that the mechanisms and energetics of electrochemical reactions at the nanoscale are quite different from those at the macroscale. Obviously, nanoscale electrochemistry appears set to revolutionize battery chemistry and lithium cells based on conversion electrodes hold much promise.

Cathode materials

Lithium-manganese spinels: The popularity of manganese dioxide in battery research dates back to one and a half centuries ago, when it was used as a 'depolarizer'. With its easy availability, low cost, non-toxicity and desirable electrochemical properties, it is probably the most exploited of battery materials. Its several forms are ideal for intercalation of small ions such as H^+ and Li^+ . Hunter⁴³ showed that the λ -form with its spinel (Mn_2O_4) framework allows reversible intercalation of lithium ions. With increasing concerns about the cost and toxicity of cobalt-based cathode (LiCoO_2), and difficulty in synthesizing phase-pure LiNiO_2 , the cubic spinel LiMn_2O_4 (Figure 4) is expected to supplant the popular LiCoO_2 cathode in commercial cells. Apart from low cost, LiMn_2O_4 offers other advantages such as high thermal threshold, excellent rate capability, and minimal health and environmental impacts. Depending on synthesis conditions and measurement techniques⁴⁴⁻⁴⁶, the chemical diffusion coefficient of lithium ions in LiMn_2O_4 can vary between 10^{-6} and 10^{-10} sq. cm/s. The capacity of LiMn_2O_4 fades upon repeated cycling, especially at temperatures

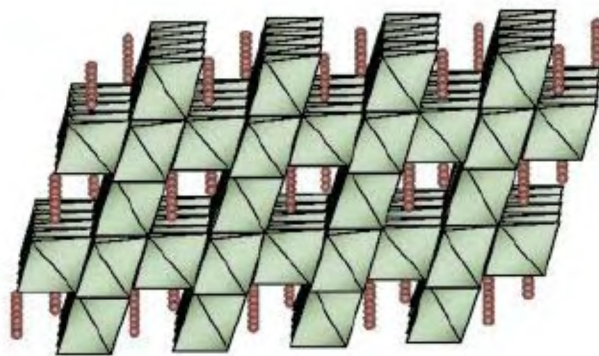


Figure 4. Structure of the cubic spinel LiMn_2O_4 .

above 55°C, primarily due to instability of the electrochemically active Mn^{3+} ion. The cathode material also gets leached in the presence of HF, which is inevitably present in trace quantities in LiPF₆-based electrolytes.

Attempts to improve the performance of LiMn_2O_4 have been directed at attaining structural stability by doping with metal ions such as Al, Co, Cr, Fe, Mg, Ni, Zn, etc.^{47–49}, and also by coating LiMn_2O_4 particles with acid-resistant materials such as ceramics, the coating levels being such that the particles should be completely covered and at the same time thin enough to allow Li^+ ion transport. But the development of an acid-free salt and/or a polymer electrolyte with high ionic conductivity seems central to commercialization of LiMn_2O_4 -based batteries. The substituents drastically change the discharge profiles, suggesting changes in the electronic structure of the spinel due to substitution⁵⁰. Ironically, our understanding of electron transport in substituted lithium manganese spinels is still limited, although it is known that the low conductivity of the spinel (10^{-4} S/cm) is due to its small polaron mechanism⁵¹. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is the most widely studied system among the substituted lithium manganese spinels^{52,53}. The presence of nickel ions stabilizes the octahedral sites⁵⁴; transition from Ni^{2+} to Ni^{4+} makes this material a 5-V cathode⁵³.

Layered lithium-metal oxides: Lithiated nickel and cobalt oxides, LiMO_2 ($\text{M} = \text{Ni}, \text{Co}$ or Ni/Co) (Figure 5) are among the most extensively studied cathodes for lithium batteries^{55–57}. Both LiNiO_2 and LiCoO_2 possess high structural stability in 3 to 4.1 V range. However, limited resources of nickel and cobalt prevent their extensive use. Accordingly, the battery industry is looking for alternatives to LiCoO_2 . Interestingly, Nissan has recently used an LiCoO_2 -derived cathode for its hybrid electric vehicle. Sanyo also developed a blend cathode of LiMn_2O_4 and

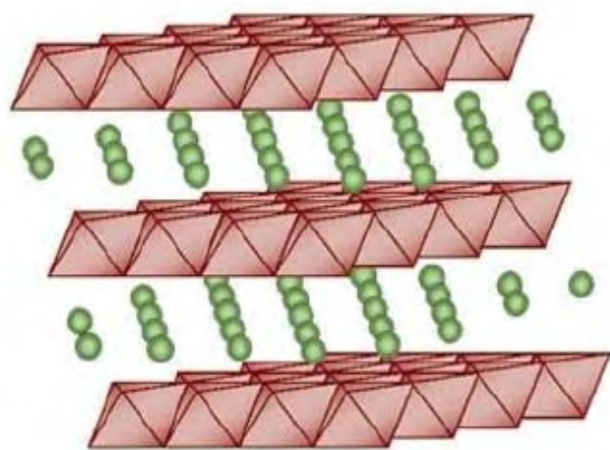


Figure 5. Structure of layered lithiated transition metal oxides, LiMO_2 ($\text{M} = \text{Ni}, \text{Co}, \text{Mn}$).

$\text{Li}(\text{Co}, \text{Ni})\text{O}_2$ with improved safety, but with lowered performance. There is, however, general consensus that solid solutions of the general formula $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ are structurally more stable than their pristine end-member homologues and also exhibit superior performance^{58–61}. According to Delmas *et al.*⁶² and Aragane *et al.*⁶³, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is a potential next-generation cathode material. We must, however, add a caveat here that given the vast disparity in the electrochemical properties of such solid solutions prepared by different routes, much care needs to be exercised in the synthesis and processing of the material.

Similar solid solutions such as $\text{Li}(\text{Co–Ni–Mn})\text{O}_2$ that combine advantageous characteristics of the individual layered compounds, LiMO_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}$), namely performance, economy, thermal stability, cost, non-toxicity, etc. are also touted as next-generation cathodes^{64–67}. $\text{LiNi}_{1-y}\text{Mn}_y\text{O}_2$, compositions isotypic with LiCoO_2 , do not lose oxygen in the charged state, and by virtue of their high capacities have drawn the attention of the industry^{65,68,69}. Kang *et al.*⁷⁰ showed by *ab initio* calculations that a combination of low-valent transition metal ions and low strain in the activated state is key to high-rate capability cathodes. They synthesized layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, with the nickel and manganese ions in the 2+ and 4+ oxidation states respectively, which delivered as much as 183 mAh/g even at 6C rate⁷⁰. In the material, Ni^{2+} acts as a double-redox active centre⁷¹ and Mn^{4+} provides stability to the host structure⁷². Although aspects such as cyclability, safety, etc. for this material are yet to be established, given its extraordinary rate capability, $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ is a potential cathode for applications requiring fast charging and discharging such as regenerative braking and portable power tools. Pacific lithium came up with a chromium analogue of this family, $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$, but the material failed to take-off because of environmental concerns associated with the use of chromium. Tadiran and Argonne National Laboratories advanced a partially lithiated MnO_2 (approximating $\text{Li}_{0.35}\text{MnO}_2$), but it was susceptible to acid-assisted disproportionation. With low toxicity, cheap raw materials, a charge voltage maximum at 3.5 V and an initial discharge capacity of at least 200 mAh/g, this material is attractive for float applications such as telecommunication. It appears that a combination of substituents that can push the thermal decomposition point of the material in the cell above 300°C, without compromising on capacity, would result in the most ideal cathode material among these solid solutions.

Vanadium oxides: These present advantages such as large capacity, high voltage and excellent kinetics for reversible lithium intercalation. However, they tend to become amorphous upon repeated cycling, which limits their applicability. Incorporation of a second metal ion such as Li^+ , Ag^+ , etc. (e.g. LiV_3O_8 , $\text{Ag}_2\text{V}_4\text{O}_{11}$) bestows structural stability to the framework^{73,74}. In fact, $\text{Ag}_2\text{V}_4\text{O}_{11}$ has been commercially exploited as a cathode in high-rate

primary lithium cells for implantable cardioverter defibrillators. In order to increase the capacity of the cathode in the region above 3 V, but without sacrificing stability, it is necessary to increase the amount of silver, which gets reduced at 3.25 V. However, silver vanadates with Ag:V ratios greater than 1:2 are poorly conducting, low-capacity cathodes⁷⁵. This problem was circumvented by replacing the oxide ions with the more electronegative fluoride ions. Sorensen *et al.*⁷⁶ showed that $\text{Ag}_4\text{V}_2\text{O}_6\text{F}_2$ delivers a 3 V capacity of 148 mAh/g as against 100 mAh/g obtainable with $\text{Ag}_2\text{V}_4\text{O}_{11}$; fluoride ions in $\text{Ag}_4\text{V}_2\text{O}_6\text{F}_2$ raised the silver reduction potential by 300 mV to 3.52 V.

Olivines: LiFePO_4 (Figure 6) has an exceptionally flat discharge plateau at 3.4 V and a moderate capacity⁷⁷ of 150–160 mAh/g. It is non-toxic and exhibits very low capacity fade, although its performance is sensitive to impurities, especially Fe^{3+} . The compound exhibits smaller volume changes and charge–discharge heat flow compared to other cathode materials. It gives optimum output at 50°C and above, restricting its use with conventional liquid electrolytes. LiFePO_4 also offers significant safety advantages over LiCoO_2 and could hence prove critical in batteries designed for high-power applications. Moreover, it is based on iron, an element that is abundant, inexpensive and environmentally benign. However, its room temperature conductivity is poor⁷⁸, of the order of 10^{-9} S/cm, and capacities close to its theoretical value may be realized only at low current densities or at elevated temperatures. The charging voltage of cells with LiFePO_4 is less than 4 V, which makes it less taxing on the electrolyte.

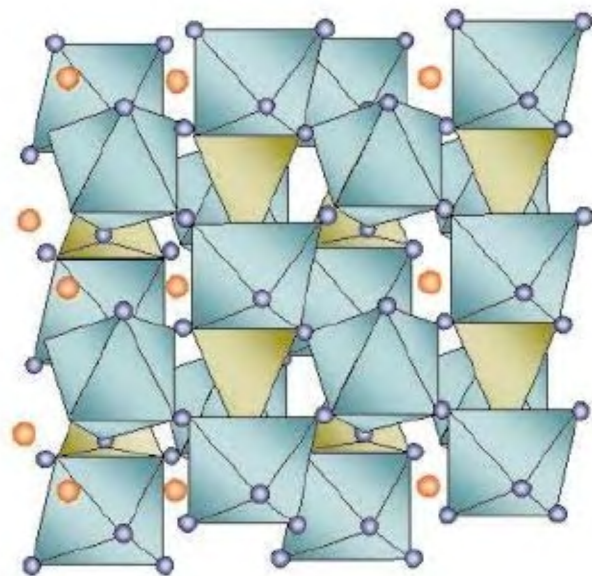


Figure 6. Olivine structure of LiFePO_4 .

Two methods have been adopted to circumvent the poor conductivity of LiFePO_4 . One is the reduction of the grain size of the cathode particle, which would lead to a diminution of the diffusion lengths both for electrons and ions, and the other is the use of nanocomposites of LiFePO_4 with a conductive matrix such as carbon. Nanocrystalline LiFePO_4 powders exhibit either high capacities (160 mAh/g) with low capacity retention⁷⁹ or low capacities (90 mAh/g) with negligible capacity fade⁸⁰. However, composites of LiFePO_4 with carbon have proved to be excellent alternatives in the search for improved LiFePO_4 cathodes^{81,82}. Recently, Takahashi *et al.*⁸³ of Nippon Telegraph and Telephone Corporation demonstrated the long-term cyclability (more than 6000 cycles) of Li/LiFePO_4 prismatic cells, as well as their outstanding thermal stability during abnormal temperature increase. Olivine-type compounds with other transition metals are difficult to synthesize and have limited capacities, although they have high discharge potentials and thus high energy output. Complex olivines such as $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, developed by Valence Technology, offer good cathode stability below 4 V.

Compounds in which the $[\text{PO}_4]^{3-}$ group is replaced with $[\text{PO}_4\text{F}]^{4-}$ group, lithium transition metal fluorophosphates, have been recently reported to be promising cathode materials. The $[\text{PO}_4\text{F}]^{3-}$ group leads to structures with altered charge balance and dimensionality compared to the corresponding phosphate⁸⁴. Ellis *et al.*⁸⁵ have reported $\text{Li}_2\text{FePO}_4\text{F}$ as a new material with facile two-dimensional transport pathways, minimal structural changes during charge–discharge and a practical capacity of 135 mAh/g. Not only does their study redefine the scope of polyanion framework materials as lithium insertion anodes, but also demonstrates the possibility of using sodium–iron phosphates as starting materials for lithium-ion battery cathodes.

A related development⁸⁶ is the possibility of a sodium-ion cell based on insertion materials such as $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$. Advantages of such cells include use of hard carbons^{87,88} with capacities of up to 350 mAh/g, improved safety, lower cost and possibility of using electrolytes up to lower decomposition voltages. Prospects for such cells are high, considering the fast-depleting terrestrial reserves of lithium, which in the short term will be used for large-capacity electric vehicle batteries that require 100–500 times the amount of lithium compared to those used in small portable cells.

Rechargeable Li_2O_2 : It is hard to imagine the design and synthesis of intercalation cathode materials with energy densities higher than twice the capacity of the present-day materials. Any concept of higher-performing materials should be based on radically different approaches such as direct reduction of oxygen from the air. In principle, oxygen cathode can lead to devices with energy densities 5–10 times higher than the current cathodes. However, only limited studies have been carried out on lithium–air non-aqueous primary cells. Ogasawara *et al.*⁸⁹

showed by *in situ* mass spectrometric studies that Li_2O_2 , the product of the electrochemical reaction between lithium and oxygen, decomposes into lithium and oxygen upon charging, a reaction that is shown to be reversible for tens of cycles. The reversibility of this reaction has tremendous ramifications in evolving a futuristic high-energy density battery. However, there are many practical issues to be addressed before anything substantial can happen in this area, including the role of catalysts, shutting-off moisture and carbon dioxide inside the cell and identification of suitable electrolytes⁹⁰.

Combustion synthesis of cathode materials: An important criterion that is often overlooked in the pursuit of mass production of batteries for applications such as electric vehicles is the viability of processes for large-volume synthesis of cathode materials. Conventional solid-state fusion methods involving repeated grinding, pelletizing and calcination are energy-intensive, time-consuming and cumbersome. Various methodologies have been developed to overcome problems of diffusion limitation associated with solid-state methods. A popular *chimie douce* method is the sol-gel method⁹¹, which usually employs expensive chemicals but cannot be profitably exploited. Another popular synthesis method is the combustion synthesis, which involves highly exothermic redox chemical species in flaming (gas-phase), smouldering (heterogeneous), or explosive reactions⁹¹⁻⁹⁷. Since the serendipitous synthesis of α -alumina by rapid heating of aluminum nitrate-urea solutions⁹⁷, much interest has been evinced in solution-based combustion synthesis of oxides. This method, also known as self-propagating, high-temperature synthesis, provides several advantages: simple, fast and energetically economic preparation, easy control of homogeneity and stoichiometry, easy incorporation of dopants/substituents, production of fine-particulate, high surface area materials by virtue of the accompanying gas evolution, and versatility in terms of the variety of fuels that can be used for the synthesis. The method has been widely used for the synthesis of cathode oxides⁹⁸⁻¹⁰². However, rapid formation of products occasionally yields less developed phases requiring subsequent calcination.

Nanostructures

There is growing evidence that nanostructured materials give improved performance compared to their bulk counterparts when used as active materials in lithium-ion batteries. It is also recognized that a key issue in the development of small, flexible batteries lies in electrode fabrication methods. Advances in the science and technology of nanomaterials and associated techniques promise a diverse variety of next-generation devices including thin-film lithium batteries. The main market driving forces for thin-film batteries are cellphones and RFID tags.

A discussion on the literature regarding nanoscopic materials for lithium battery applications is beyond the scope of this article. However, a brief account of special features of nanomaterials for battery applications would not be out of place. The small particle size of nanoscale materials allows dramatically short diffusion distances, which translate into high rate capability of active materials and increased capacity utilization. Their large surface areas allow quick absorption of sizeable amounts of lithium ions without structural deterioration. However, the increased reactivity arising from high surface area enhances the reaction of active materials with the electrolyte, which can prove detrimental to cell performance.

Carbon nanotube-based active materials are known to exhibit remarkably high capacities. A number of other nanomaterials have also been investigated. For example¹⁰³, mechanically milled nanometric Sn-Fe-C alloys have been shown to cycle well with reversible capacities of 1600 mAh/g. Nanocomposites of silicon and carbon are another interesting class of materials. A nanocomposite of silicon with carbon black¹⁰⁴ gave capacities as high as 1700 mAh/g, while one with mesocarbon microbeads¹⁰⁵ was shown to give 1066 mAh/g. Wang *et al.*¹⁰⁶ showed that nanosized Co_3O_4 gives a higher lithium storage capacity (780 mAh/g in the first cycle) than a normal crystalline sample of Co_3O_4 .

A nanocrystalline NiSi alloy was shown to give a lithium storage capacity of 1180 mAh/g, although the capacity faded with cycling¹⁰⁷. Another alloy, Ni_3Sn_4 , exhibited an initial lithium insertion capacity of 1515 mAh/g that cannot be related to simple alloying reactions¹⁰⁸. Wang *et al.*¹⁰⁹ demonstrated the significantly different electrochemical properties of WS_2 nanotubes compared to WS_2 powders. The nanotubes gave lithium insertion capacities of 915 mAh/g, corresponding to an intake of 8.6 Li per formula unit of WS_2 . This is significantly higher than the 0.6 Li per formula unit equivalent capacity delivered by WS_2 powder electrodes.

The poor electrochemical properties of LiFePO_4 , an otherwise attractive cathode material, are related to its poor conductivity and low diffusivity for lithium ions¹¹⁰. Yet nanocomposites of LiFePO_4 have been shown to exhibit excellent performance. Singhal *et al.*⁸¹, who investigated a variety of nanostructured electrode materials, found that V_2O_5 particles with a metastable structure show 30% higher retention capacity compared to their coarse-grained counterparts and that ultrafine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows less than 10% capacity fade over 70 cycles at a discharge rate of 10C. Kavan *et al.*¹¹¹ have established a correlation between particle size and complete charging period for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by which it is possible to reduce the charging period of practical cells to a matter of minutes.

A switch from bulk morphologies to the nanoscale has been shown to bring about dramatic changes in the elec-

trochemical performance of TiO_2 . The anatase form of the oxide can deliver 165 mAh/g, corresponding to a lithium intake of 0.5 Li per TiO_2 unit¹¹². However, Armstrong *et al.*¹¹³ showed that nanowires of TiO_2 (B) delivered capacities of up to 305 mAh/g for many cycles. The upgraded capacity value corresponds to a lithium intake of 0.9 Li. Similarly, dramatic improvement in electronic conductivity was recorded with nanocrystalline $\text{LiM}_y\text{Fe}_{1-y}\text{PO}_4$ ($M = \text{Mg, Zr, Ti}$) compositions¹⁰⁸. At a discharge rate of C/8, both undoped and titanium-doped nanocrystalline LiFePO_4 gave stable discharge capacities of 160–165 mAh/g, almost approaching the theoretical value¹¹⁴. Cheng *et al.*¹¹⁵ showed that HClO_4 -doped polyaniline (PANI) nanofibres exhibited higher electrical conductivity and better cycling capability compared to commercial doped powders. This finding augurs well for the realization of Li/PANI rechargeable batteries.

In a complete study on the relationship between the structure and electrochemical behaviour of nanostructured materials, Okubo *et al.*¹¹⁶ studied the electrochemical lithium insertion behaviour of precisely-sized LiCoO_2 synthesized by a hydrothermal method. The authors showed that as the crystallite size decreased, capacitor behaviour become dominant. For example, as the crystallite size was decreased from 17 to 8 nm, the capacity contribution¹¹⁶ increased from 2.6 to 6.4 mAh/g. Interestingly, the charging (deintercalation) potentials decreased with size. The lower potentials suggest the effect of nanosize on the electrochemical performance of LiCoO_2 . Apparently, the structural property of nanomaterials is different from the bulk materials. Okubo *et al.*¹¹⁶ also demonstrated the good high-rate performance of nanocrystalline LiCoO_2 up to 100C rate, although extreme size reduction (below 15 nm) proved detrimental to cathode performance. The cycling performance of nanosized LiCoO_2 was, however, much inferior to that of a bulk sample, which they attributed to the enhanced reactivity of the high surface area material.

The beneficial effect of nanoscopic materials as inert fillers has been demonstrated with PEO-LiClO_4 electrolytes. Ahn *et al.*¹¹⁷ showed that nanosize TiO_2 particles in the electrolyte enhanced its conductivity by a factor of two. According to them, the large surface area of the particles prevents reorganization of PEO chains at room temperature. TiO_2 contains hydrophilic surface groups such as $-\text{COOH}$ and $-\text{OH}$. These polar groups interact with the anions and the PEO segments. The interaction reduces ion aggregation, which increases the fraction of free lithium ions and enhances the conductivity. The inert filler also acts as a 'solid plasticizer', which reduces polymer crystallinity enhancing transport properties¹¹⁸. According to the effective medium theory, the highly conductive interface layer between the PEO matrix and the nanoparticles can contribute to increased conductivity¹¹⁹.

Thin-film lithium batteries

Thin-film batteries or nano energy devices, as they are sometimes called, are thinner than a sheet of paper. Being thin, they can be embedded in microdevices, in which they can serve as autonomous power sources. Such batteries are expected to open up avenues for a variety of self-powered microdevices. Thin-film solid-state batteries are made by depositing thin films (less than 5 μm) of the components on a substrate: a cathode such as Sn_3N_4 sputtered on a substrate, a layer of Lipon electrolyte-cum-separator sputtered on the cathode followed by a thermally evaporated layer of lithium. Such next-generation, ultra-thin rechargeable batteries are projected for card-type applications. By increasing the porosity and reducing particle size, the effective surface area of electrodes can be enhanced 1000–100,000 times without affecting their geometrical dimensions. The resulting high surface areas can permit high current drains.

Nexelion batteries

Sony recently unveiled a hybrid lithium-ion rechargeable battery that it christened as Nexelion batteries¹²⁰. The anode is a tin-based amorphous material consisting of multiple elements such as tin, cobalt, carbon, etc. in nanoscopic sizes. The presence of several elements in the tin-based compound ensures little change in particle shape and size during charge and discharge. The new material provides a lithium ion density that is 50% higher than that in conventional graphite (Figure 7). Owing to its higher affinity for lithium ions (compared to graphite), the new battery has a 20% higher charging efficiency than that of the conventional battery. Moreover, the Nexelion battery can be charged to 90% of its capacity in a matter of 30 min.

A biological approach

There is evidence that use of nanostructured active materials can result in high-performance lithium-ion batteries,

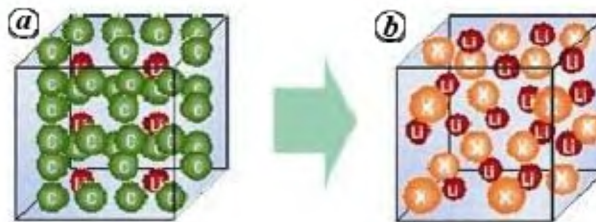


Figure 7. *a*, Lithium ion distribution in conventional graphite anode. *b*, Sony's amorphous anode containing nanosized particles of tin, cobalt, carbon, etc. minimizes shape changes during charge and discharge. This results in 50% higher lithium ion density than in graphite-based anode⁸⁸.

and that such materials must be present in monodispersed, homogeneous and hierarchical organization so as to maximize the benefits. It is known that biosystems, with their capability for molecular recognition and self-assembly, can be attractive templates for producing such nanoarchitectures. Investigations have, therefore, been directed at designing hierarchical self-assembled batteries^{121–123}. In one such study, researchers at the Massachusetts Institute of Technology, USA designed a rechargeable lithium-ion battery assembled from microscopic materials¹²¹. Their prototype battery consisted of LiCoO_2 and microbeads of graphite, and could be cycled multiple times. It is believed that the new approach would translate into ultra-small power sources for sensors and micro-machines. It could also be used to pack battery materials in unused space inside electronic devices.

Electrolytes

It is well recognized that a sustainable battery technology depends on a robust electrolyte that can support high-performance electrodes. On that count, any discussion on electrolytes must be predicated on the interdependence of the performance characteristics of the active materials and electrolyte properties. Organic, aprotic, solvent-based liquid electrolytes for lithium batteries come in various forms: simple solutions, solutions held in the pores of a membrane, gels made of polymer, solvent and salt, and solvent-less gels. A common electrolyte solution is LiPF_6 in EC–DEC–DMC, which according to Aurbach *et al.*¹²⁴, is only a compromise, for it is not only flammable but also has electrochemical stability up to only about 4.5 V. Alternatives to such alkyl carbonate solvents are not on the horizon, although lithium bis(oxalato)borate, LiBC_4O_8 (LiBOB), and lithium fluoroalkylphosphates (e.g. $\text{Li}[\text{PF}_3(\text{C}_2\text{F}_5)_3]$) are being considered in place of LiPF_6 . A weaning away from LiPF_6 is also on the cards as the industry pushes towards less expensive cathode materials such as those based on manganese. Alkylated derivatives of LiPF_6 can be made in acid-free state, but high solution viscosities and molecular weights can reduce electrolyte conductivity. LiBOB is promising, but obtaining high-purity salt is difficult. Lithium triflates are another class of promising salts, but they corrode battery casing and current collectors. Aurbach *et al.*¹²⁴ suggest that under these circumstances, it is only prudent to investigate additives that can protect electrode-active materials even at high temperatures by forming highly protective films on the electrodes. Recently, however, it was demonstrated that liquid electrolytes based on complexes with BF_3 can have high electrochemical stability windows. For example, a LiPF_6 -based electrolyte in a complex of BF_3 with 2-methyl tetrahydrofuran not only had higher ionic conductivity¹²⁵, but also was oxidatively stable up to 5.8 V vs Li^+/Li .

Polymer electrolytes

Ionically conductive polymers are the Holy Grail for large and safe lithium-ion batteries. The applicability of PEO-based polymers is limited to 3.5 V. Modified polymers such as polyimines and polyimides have been suggested, but their cost can be forbidding. The poor thermal stability of LiPF_6 limits its use in polymer electrolytes that work between 50 and 80°C. However, its analogue, the stable LiAsF_6 , is toxic, while LiBF_4 has a relatively low voltage limit. Imides with wide thermal and voltage windows are also a choice. In fact, $\text{Li}(\text{SO}_3\text{CF}_3)_2$ (LiTFSI) appears promising due to its high stability and high conductivity. Composite polymer electrolytes based on nanoparticles of ceramics exhibit higher conductivity and are apparently resistive towards high-voltage oxidation. Improved electrical and mechanical properties have been realized with polymer-silicate nanocomposites in which nanoscale clay particles are molecularly dispersed within a polymeric matrix¹²⁶.

A notable advancement in the area of polymer electrolytes is the development of a non-flammable polymer electrolyte¹²⁷. The development is significant given the several battery ‘flashing’ accidents in the recent past involving flammable organic electrolyte-based batteries. Even commercially available polymer electrolyte batteries are not free from fire hazard as they contain flammable organic liquids. Development of a non-flammable polymer electrolyte battery is thus crucial. Bakenov *et al.*¹²⁷ demonstrated such a system with an electrolyte based on poly(ethylene glycol) borate. They also employed AlPO_4 as an additive in the electrolyte, which led to a stabler electrode–electrolyte interphase, thereby enhancing the rate capability of the cell¹²⁷.

Polymer electrolytes also permit the use of lithium metal as a rechargeable anode. It is known that PEO-based gel electrolytes suppress dendritic deposits on the lithium anode owing to the immobility of the electrolyte^{128–130}. Osaka and Momma¹³¹ employed an electrolyte based on PVdF–HFP, which they found led to the formation of a protective layer on the metal due to a reductive reaction with the polymer. A further modification of the lithium surface with CO_2 added to the electrolyte led to smooth surface films with reduced impedance^{132,133}. These studies open up possibilities of employing lithium metal as anodes in practical rechargeable cells.

Non-flammable electrolytes

Solvents used in lithium-ion batteries are typically low-boiling and have flash points around 30°C. Therefore, a major danger lurks from a cell that vents or explodes due to the flammability of the spewing hot electrolyte vapours. Accordingly, much effort is being expended on developing ‘low flammability’ or ‘flame retarding’ electrolytes that

do not support continued combustion when the source of heat, spark or flame is withdrawn. It is also important to ensure that the heat of reaction of the electrolyte with the charged electrode should also be low to prevent any self-sustaining combustion reaction under accidental heating. Present-day electrolyte formulations are actually a trade-off between their flammability and cell performance. The fall in cell performance is due either to electrochemical instability that leads to capacity fade or increased viscosity of the additive, which leads to reduced ionic transport and hence to lower capacity utilization and power. Since performance cannot be sacrificed, studies mostly focus on flame-retardants as additives or co-solvents in known electrolyte formulations^{133–135}. Fluorinated compounds¹³⁴ and organo-phosphorus compounds^{134,135} are among the most investigated co-solvents to mitigate flammability. For example, trimethyl phosphate, a popular flame-retardant, has been studied for its electrochemical stability on the positive and negative electrodes of lithium-ion cells^{134,135}. It is noteworthy that since electrolytes react with the active materials in lithium-ion batteries, the surface chemistry at the anode and cathode is central to cell performance. Therefore, the design of new electrolytes must also consider the properties of the solid electrolyte interphase at the electrodes.

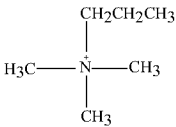
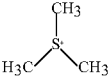
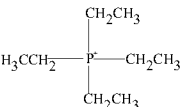
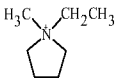
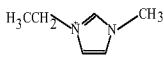
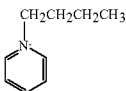
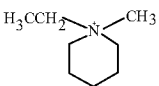
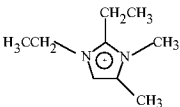
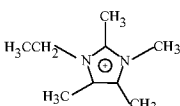
Ionic liquids

Room-temperature molten salts, also known as ionic liquids, are a new class of materials that are expected to provide solutions to the aforesaid problems. Most notably, they exhibit desirable properties expected for lithium-ion electrolytes, namely wide liquid range (allows cell operation in a wide temperature range), low volatility (makes for easy handling and also prevents electrolyte drying), non-flammability (improves device safety), decomposition temperatures above 300°C (aids in high-temperature operation), wide electrochemical window (enhances power and energy densities), and low heat of reaction with active materials (leads to improved cell safety). Several ionic liquids are oxidatively stable even at 5 V, though their reductive stability could be poor. One of the central issues is identification of ionic liquids with sufficient lithium-ions to allow high flux of lithium ions through the electrolyte. There are two major types of ionic liquids: one containing imidazolium cation and the other containing quaternary ammonium (or phosphonium) cation (Table 1).

Ionic liquids based on the EMI (1-ethyl-3-methylimidazolium) cation are attractive because of their low viscosities, but they react with lithium and even dissolve intercalated lithium out of graphite¹³⁶. EMI-BF₄ has a reduction potential of about 1 V vs Li⁺/Li, but the reduction potential of the EMI⁺ cation can be tailored by incorporation of organic functional groups¹³⁷. For example, 1,2-

diethyl-3,4(5)-dimethylimidazolium tetrafluoroborate exhibits very little decomposition at 0 V vs Li⁺/Li and is stable over a wide electrochemical window (up to 5 V vs Li⁺/Li)¹³⁷. Additionally, it has a relatively low melting point of about 20°C and a specific conductivity of 1.44×10^{-3} S/cm at 20°C. Nakagawa *et al.*¹³⁸ demonstrated that the conductivity of mixtures of EMI-BF₄ with LiBF₄ increases with increasing quantities of LiBF₄, reaching as much as 1×10^{-3} S/cm. Additionally, increased amounts of LiBF₄ reduce the melting point of the mixture. They also showed¹³⁸ that such mixtures are stable even at 300°C. Quaternary ammonium cations are another class of compounds that can withstand reduction at the anode.

Table 1. Cations and anions that comprise commonly employed ionic liquids

Cation	Structure
Trimethylpropylammonium	
Trimethylsulfonium	
Tetraethylphosphonium	
Ethylmethylpyrrolidinium	
1-Ethyl-3-methylimidazolium	
Butylpyridinium	
N-Methylpiperidinium	
1,2-Diethyl-3,4(5)-dimethylimidazolium	
1-Ethyl-2,3,4,5-tetramethylimidazolium	

Anions: AlCl₄⁻, BF₄⁻, CH₃BF₃⁻, C₂F₅BF₃⁻, CF₃SO₃⁻, N(CF₃SO₂)₂⁻, N(SO₂CF₃)₂⁻, PF₆⁻.

Sakaebe and Matsumoto¹³⁹ have shown higher Coulombic efficiency and larger utilization of the positive electrode as well as improved safety with an *N*-methyl-*N*-propylpiperidinium-bis(trifluoromethanesulfonyl)imide electrolyte.

By virtue of its small size, Li⁺ ion behaves as a strong Lewis acid and interacts strongly with anions in salts, which results in salts with high melting point and high viscosity. Fujinami and Buzoujima¹⁴⁰ designed ionic liquids containing weakly coordinating anions, which not only lowered the melting points but also promoted dissociation. However, viscosities of the salts are too high to be employed in practical lithium cells. Shin *et al.*¹⁴¹ showed that the conductivity of a (PEO)₂₀-(CF₃SO₂)₂NLi electrolyte could be raised from 2×10^{-6} to 1×10^{-4} S/cm at 20°C by incorporating *N*-methyl-*N*-propylpyrrolidinium-(CF₃SO₂)₂N in it. Test cells with this electrolyte have been found to sustain about 500 charge-discharge cycles¹⁴¹. Recently, a gelled form of ionic liquid electrolyte with a polymer was reported for dimensional stability¹⁴². Egashira *et al.*¹⁴³ showed that the cycling performance of non-cyclic quaternary ammonium-based ionic liquids could be improved by introducing cyano groups. It is hoped that with sustained research an ionic liquid electrolyte with desirable safety and electrochemical characteristics will emerge.

Organic radical battery

Organic radicals are unstable and intractable species. Nakahara *et al.*¹⁴⁴ and Nishide *et al.*¹⁴⁵ have demonstrated the use of organic radical polymers as electroactive materials, opening up a new area of organic radical batteries. A nitroxide radical polymer such as poly[2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate] (PTMA) with a molecular weight $>10^4$ has almost 100% radical content. It has a T_g (glass-transition temperature) value of 70°C and the radicals on PTMA are almost stable up to its thermal decomposition temperature of 263°C. The polymer is soluble in certain organic solvents, which makes it amenable to processing via wet, printing and roll-tape techniques. At the same time, it is insoluble in battery electrolytes such as ethylene carbonate and diethyl carbonate containing LiPF₆, which is critical for its exploitation as a cathode material. However, to overcome its poor conductivity, it is mixed with 20–50% graphite.

Lithium cells containing PTMA show plateau voltages of 3.5 V and at a discharge rate of 1C deliver capacities of 110 mAh/g, which is close to 100% of its theoretical value (111 mAh/g). Besides, at 10C discharge, these cells retained 95% of the charging capacity obtainable at 1C. The cells could be charged quickly, in a matter of just 5 min, and could be discharged at 50C rate with almost no voltage drop or capacity loss. The excellent rapid charge-discharge characteristics make these cells attractive for

electric vehicle applications. The cells also display little self-discharge. Furthermore, no significant capacity fade is observed during a cycling regime lasting more than 1000 cycles. The long cyclability of the cathode is attributed to the chemical stability of the nitroxide radical as well as to the absence of structural changes in the organic polymer during the charge-discharge processes. Such organic active materials promise high-performance and durable batteries that are light, thin, flexible and environmentally benign. The fact that the nitroxide radical polymer is completely combustible to yield only carbon dioxide, water and a small amount of nitrogen oxide is another attractive feature of this material. Furthermore, avoiding the use of metals in the cathodes helps in conserving the dwindling metal resources.

Safety aspects

The Gibbs-Helmholtz equation relates the temperature derivative of the free energy change, ΔG , for a reaction to the associated change in entropy, ΔS , as follows.

$$[d(\Delta G)/dT]_{p,n(i)} = -\Delta S, \quad (1)$$

where T is the absolute temperature.

ΔG for an electrochemical reaction is expressed as

$$\Delta G = -nFE, \quad (2)$$

where n is the number of electrons transferred, F the Faraday and E the voltage corresponding to the electrochemical reaction. Thus,

$$\Delta S = nF(dE/dT)_{p,n(i)}. \quad (3)$$

Since

$$\Delta G = \Delta H - T\Delta S, \quad (4)$$

where ΔH is the enthalpy of the reaction,

$$\Delta G = \Delta H - nFT(dE/dT). \quad (5)$$

If dE/dT is positive, the cells will heat on charge and cool on discharge. Nickel-cadmium battery is an example with a negative dE/dT , making the cell cool on charge and heat up on discharge. Lead-acid is an example with positive dE/dT that makes the cell to heat on charge and cool on discharge. Lithium-ion batteries have a negative dE/dT , which means they can overheat during high-current drains. Heating and cooling of cells can proceed with heat exchange with the environment.

In general, the entropy heat, $T\Delta S$, is negligibly small compared to the irreversible heat, q , which is released when the cell is in operation. The following equation

$$q = T\Delta S + I(E_{\text{OCV}} - E_T) \quad (6)$$

describes the total heat released, including the reversible thermodynamic heat released along with the irreversible Joule heat from operation of the cell in an irreversible manner, during charge or discharge at finite current/rate. In eq. (6), E_T is the terminal voltage and E_{OCV} is the open-circuit voltage. Irreversible behaviour manifests itself as a departure from the equilibrium or thermodynamic voltage. The total heat released during cell discharge is the sum of the thermodynamic entropy contribution and the irreversible contributions. This heat is released inside the battery at the reaction site on the surface of the electrode structure. Heat release is not a problem for low-rate applications where heat dissipation exceeds heat generation. However, high-rate batteries must make provisions for heat dissipation. Failure to accommodate/dissipate heat appropriately can lead to thermal runaway and other catastrophic situations. Overheating of batteries may be prevented by use of conventional current-limiting devices such as safety vents, fuses, positive coefficient devices, temperature cut-off devices and protection circuit modules as well as by the use of shutdown separators, shutdown additives, redox shuttles and coatings.

Shutdown additives can either release gases, which in turn activate a current interrupter device, or undergo polymerization, thereby blocking ion transport in the electrolyte. Gas-releasing shutdown additives being investigated include biphenyl, cyclohexylbenzene and pyrocarbonates¹⁴⁶. Biphenyl and other substituted aromatic compounds constitute the polymerizable class of shutdown additives¹⁴⁷.

Redox shuttles are among the most promising mechanisms for overcharge protection¹⁴⁸. The working of redox shuttles added to electrolytes, involves electrochemical oxidation of a species at one electrode, which then diffuses to the other electrode where it gets reduced (Figure 8). The selection of 4 V cell shuttles for lithium-ion cells presents a challenge as only a handful of substances are

amenable to reversible turnover at potentials around 4 V vs Li^+/Li . These include complexes of cerium, iridium, iron or ruthenium with phenanthroline or bipyridine. Their redox potentials can be tuned by varying the number, nature and position of substituents on the aromatic rings¹⁴⁹. However, problems of low shunt currents, due partly to their limited solubilities in non-aqueous electrolytes and partly to the low diffusion coefficients resulting from their large sizes and molecular weights, remain to be tackled. Adachi *et al.*¹⁴⁹ suggest that a structure–property relationship in these molecules would help in the design and selection of efficient redox shuttles.

Thermal stability of the electrolyte in contact with active materials is of great concern in lithium-ion batteries. Improvement of thermal stability by encapsulating active material particles has been applied to both anode and cathode active materials. For example, Yoshio *et al.*¹⁵⁰ showed that coating carbon on graphite can effectively suppress the decomposition of propylene carbonate on the anode as well as subsequent exfoliation of graphite. Cho *et al.*¹⁵¹ demonstrated that LiCoO_2 coated with AlPO_4 blocks thermal runaway of lithium-ion cells in addition to significantly reducing electrolyte oxidation and cobalt dissolution into the electrolyte. Fey *et al.*¹⁵² showed that LiCoO_2 coated with cobalt oxides displays increased resistance to decomposition reactions with the electrolyte. Such coatings not only lead to an increase in thermal stability, but also in the cycle life of cathodes.

Separators are also central for the safety of lithium-ion batteries. In addition to conventional characteristics such as chemical resistance, mechanical strength, microporosity, and electrolyte permeability, separators must display a protective property during cell abuse¹⁵³. For example, in cells that use separators made with laminating layers of polypropylene/polyethylene/polypropylene (PP/PE/PP), any abnormal rise in cell temperature would soften PE (m.p. 135°C), resulting in the closure of micropores in the film. This is called separator ‘shutdown’^{154,155}. Once shutdown occurs, ionic transport between the electrodes is effectively stopped and current ceases to flow. However, the separator should retain mechanical integrity above its shutdown temperature in order to provide a margin of safety to the device; otherwise, the electrodes can come into direct contact, react chemically, leading to thermal runaway. This is provided by polypropylene (m.p. 165°C). Shutdown separators are increasingly being used by lithium battery manufacturers.

Conventional polyolefin separators have porosities¹⁵⁶ of about 40%. The limited uptake of the electrolyte can restrict the performance of the cell. Cho *et al.*¹⁵⁷ recently demonstrated the use of polyacrylonitrile (PAN) nanofiber-based non-woven separators for use in lithium-ion batteries. These separators had porosities as high as 76%. Moreover, the PAN non-woven separators are stable up to at least 250°C, which means their use would enhance the stability of the cell. Cho *et al.*¹⁵⁷ also demonstrated

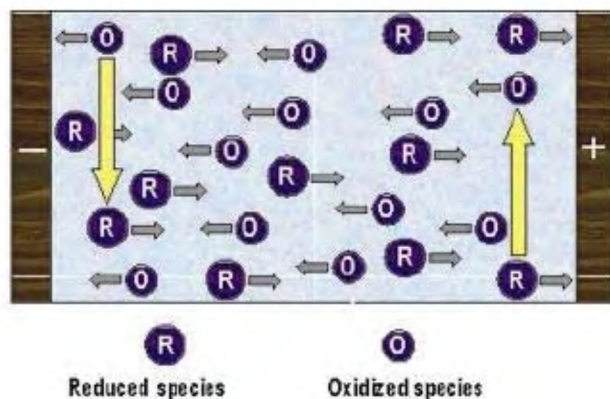


Figure 8. Schematic of the working of redox shuttles. Compound R gets oxidized at the positive electrode to O , which diffuses to the negative electrode and gets reduced to the original molecule R .

the improved performance of cells with these separators compared to those with conventional separators. The improved electrochemical performance is ascribed to higher ionic conductivity resulting from the higher electrolyte uptake of liquid electrolyte¹⁵⁸. Ceramic composite separators based on non-woven polyolefin microporous fibres (PE/PP) and hydrophilic SiO₂ powder (7 nm) were recently shown to have improved performance in terms of thermal stability, wettability and cell capacity¹⁵⁹. A significant effect of incorporation of ceramic filler in the membrane electrolyte is the much lowered shrinkage of the separator upon heating. As compared to a shrinkage of 37.5% along the machine direction for a Celgard PP separator, the ceramic-filled membrane showed only 3% shrinkage¹⁵⁹.

Electric vehicle applications

While continual evolution and sophistication of portable electronic gadgets drive research and development of new materials and power systems, there is mounting pressure for speedy replacement of the energy-guzzling internal combustion engine vehicles with electric or hybrid electric vehicles. This is necessitated by the progressive depletion of oil resources and increasing concerns for preserving the quality of air that sustains life on this planet. Batteries are an ideal answer for automobiles with zero emission (electric vehicles) or controlled emission (hybrid electric vehicles). In the near term, however, only electric scooters/motorcycles are poised to promote large-scale moves towards electric vehicles. Lithium batteries, with an average operational cell voltage of 3.5 V and energy densities ranging from 150 to 250 Wh/kg, are most suitable for such applications. However, such high-capacity configurations must meet customer demands such as safety and affordability. Researches in this direction are aimed at finding: (i) alternative materials to carbon anode with higher capacity, (ii) environmentally benign alternatives to LiCoO₂ with low-cost, and (iii) safer polymer electrolytes¹⁶⁰ as alternative to the organic liquid electrolytes.

Intermetallics are considered potential replacements for the carbon electrode. Nickel–tin active–inactive matrix is among the most promising materials with practical capacities in the 500-plus mAh/g range^{161,162}, although their long-term cyclability is not established²⁹. It is felt that improvements could be affected by the use of nanostructured alloys¹⁶³ that can lead to lower overall stress during cycling. Furthermore, the free volume in nanostructures can buffer volume changes that accompany the charge–discharge processes. However, the increased reactivity at the nanoscale and reduction in energy density due to availability of free volume in such structures calls for innovative electrode designs. Among the cathode materials are lithium olivines, the most representative candidate being LiFePO₄. High-voltage lithium–nickel–manganese

spinel, LiNi_{0.5}Mn_{1.5}O₄, is another candidate vying for attention. The challenge in the area of plastic electrolytes is to obtain compatible, free-standing polymer electrolytes whose conductivity values are reminiscent of liquid electrolytes.

Outlook

Potential next-generation active and passive materials for lithium battery systems have been reviewed. It is clear that advances in battery materials in terms of their capacity, reversibility, rate capability, and thermal and electrochemical stability should lead to devices that outsmart currently available systems. The bottom line for manufacturers and users has to do with affordable, safe and environment-friendly batteries with greater energy and power, in conjunction with long life. To this end, new high-performance materials are desirable. Specifically, these include anode materials based on novel carbon varieties such as kish graphites and nanostructured carbons including carbon nanotubes. Several lithium-alloying intermetallics as well as thin-film silicon-based anodes are also on the horizon. A large variety of cathode materials are also gearing up for commercialization. These include layered Li(Co/Ni)O₂, Li(Co/Ni/Mn)O₂ and Li(Mn/Ni)O₂ oxides, inexpensive LiMn₂O₄ spinel derivatives, highly stable LiFePO₄ and other olivines. As for electrolytes, the focus will be on replacing LiPF₆ with LiBOB or triflates, and development of suitable room temperature molten salts. Replacement of present-day separators with thermally more stable and high-porosity separators with good wetting properties should lead to safer and higher rate batteries. There is emerging thrust towards exploiting nanoscience and nanotechnology, which calls for large-scale production of battery materials as well as engineering breakthroughs towards miniature batteries, including embedded power packs. There is already enough indication that electrochemistry at the nanoscale needs to be redefined, which means that a new world of challenges and opportunities beckon the initiated. It is believed that the marriage of novel cell chemistries and new technologies will eventually culminate in a superior lithium battery¹⁶⁴.

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