

Building better batteries

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Researchers must find a sustainable way of providing the power our modern lifestyles demand.



Batteries are currently being developed to power an increasingly diverse range of applications, from cars to microchips. How can scientists achieve the performance that each application demands? How will batteries be able

to power the many other portable devices that will no doubt be developed in the coming years? And how can batteries become a sustainable technology for the future?

The technological revolution of the past few centuries has been fuelled mainly by variations of the combustion reaction, the fire that marked the dawn of humanity. But this has come at a price: the resulting emissions of carbon dioxide have driven global climate change. For the sake of future generations, we urgently need to reconsider how we use energy in everything from barbecues to jet aeroplanes and power stations.

If a new energy economy is to emerge, it must be based on a cheap and sustainable energy supply. One of the most flagrantly wasteful activities is travel, and here battery devices can potentially provide a solution, especially as they can be used to store energy from sustainable sources such as the wind and solar power.

Because batteries are inherently simple in concept, it is surprising that their development has progressed much more slowly than other areas of electronics. As a result, they are often seen as being the heaviest, costliest and least-green components of any electronic device. It was the lack of good batteries that slowed down the deployment of electric cars and wireless communication, which date from at least 1899 and 1920, respectively (Fig. 1). The slow progress is due to the lack of suitable electrode materials and electrolytes, together with difficulties in mastering the interfaces between them.

All batteries are composed of two electrodes connected by an ionically conductive material called an electrolyte. The two electrodes have different chemical potentials, dictated by the chemistry that occurs at each. When these electrodes are connected by means of an external device, electrons spontaneously flow from the more negative to the more positive potential. Ions are transported through the electrolyte,

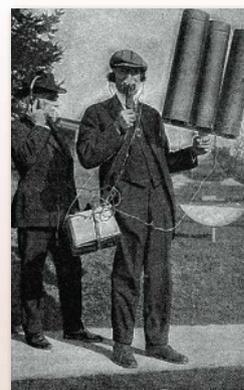
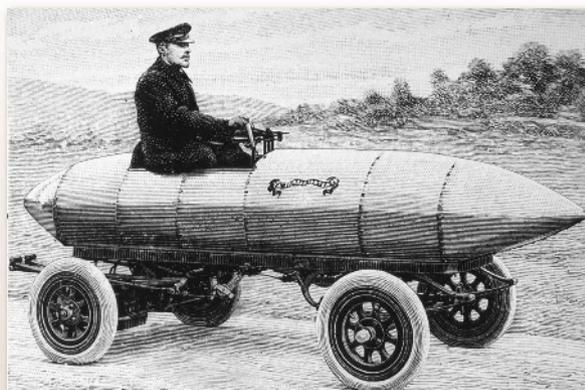


Figure 1 | Revisiting the past. In 1899 a Belgian car, *La jamais contente* (top left), equipped with lead–acid batteries, reached a speed of 30 metres per second (ref. 26). In the same year, at a car competition in Paris, the only petrol-driven car was disqualified for having unpractically high consumption. Inside the United States, between 1900 and 1920, the proportion of electrical cars produced fell from 60% to 4% of the total. One century later, fully electrical cars, such as the Tesla roadster (bottom left), are coming back into the picture. Meanwhile, the first wireless communication took place in Pennsylvania in 1920 (top right, after ref. 27). Nearly 100 years later, the latest mobile phones (bottom right) can perform a wide range of functions.

maintaining the charge balance, and electrical energy can be tapped by the external circuit. In secondary, or rechargeable, batteries, a larger voltage applied in the opposite direction can cause the battery to recharge.

The amount of electrical energy per mass or volume that a battery can deliver is a function of the cell's voltage and capacity, which are dependent on the chemistry of the system. Another important parameter is power, which depends partly on the battery's engi-

neering but crucially on the chemicals the battery contains. Hundreds of electrochemical couples were proposed during the nineteenth and early twentieth centuries, the most notable primary battery being Zn–MnO₂, with lead–acid and Ni–Cd being the most common secondaries¹.

The stored energy content of a battery can be maximized in three ways: (1) by having a large chemical potential difference between the two electrodes; (2) by making the mass (or

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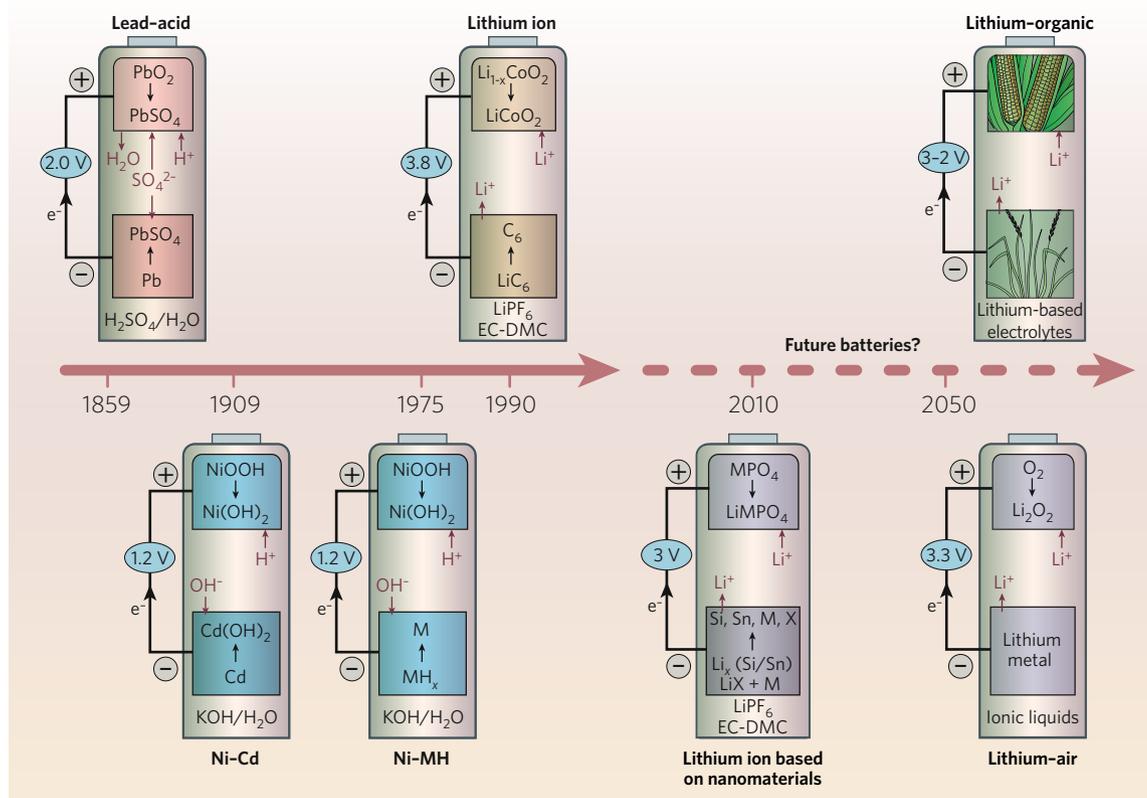


Figure 2 | Battery chemistry over the years. Present-day battery technologies are being outpaced by the ever-increasing power demands from new applications. As well as being inherently safe, batteries of the future will have to integrate the concept of environmental sustainability.

volume) of the reactants per exchanged electron as small as possible; and (3) by ensuring that the electrolyte is not consumed in the chemistry of the battery. This final condition was not true of the three principal battery technologies developed in the twentieth century, but holds for the more recent Ni–MH and lithium-ion batteries. One of the key elements of these two batteries is that the same ion (H^+ for Ni–MH and Li^+ for lithium-ion batteries) participates at both electrodes, being reversibly inserted and extracted from the electrode material, with the concomitant addition or removal of electrons. Ni–MH batteries are used to power hybrid vehicles and cheaper electronics, whereas lithium-ion batteries have conquered high-end electronics and are now being used in power tools. Lithium-ion batteries are also entering the hybrid electric-vehicle market and are a serious contender to power the electric cars of the future.

The lithium-ion battery, first commercialized by Sony in 1991, owes its name to the exchange of the Li^+ ion between the graphite (Li_xC_6) anode and a layered-oxide ($Li_{1-x}T^MO_2$) cathode², with T^M being a transition metal (usually cobalt but sometimes nickel or manganese). The energy it stores ($\approx 180 \text{ Wh kg}^{-1}$) at an average voltage of 3.8 V is only a factor of 5 higher than that stored by the much older lead–acid batteries. This may seem poor in the light of Moore’s law in electronics (according to which memory capacity doubles every 18 months), but it still took a revolution in materials science to achieve it.

Billions of lithium-ion cells are produced for portable electronics, but this is not sustainable as cobalt must be obtained from natural

resources (it makes up 20 parts per million of Earth’s crust^{3,4}). In addition, there are safety concerns, as the presence of both combustible material and an oxidizing agent carries a risk of runaway reactions resulting in fires or explosions. Improvements in the electrolyte composition could make the chemistry safer, but accidents are mainly a result of fierce cost-cutting and attempts to cram more active material in the same volume, causing internal short-circuits. As a result, improvements in monitoring and management are essential if lithium-ion batteries are to fulfil their potential in the automotive market.

Lithium-ion batteries would also need to reduce their carbon footprint, which is currently about 70 kg CO_2 per kWh (ref. 5). The carbon-related benefits of electric vehicles or ‘plug-in hybrids’ become apparent only after around 120 recharges with respect to electricity from coal, assuming a power-plant efficiency of 35% and that the batteries replace a petrol engine in which 20% of the heat from combustion is converted into useable energy. However, these break-even numbers need to be reduced.

Replacing each of the world’s 800 million cars and lorries with electric vehicles or plug-in hybrids powered by 15-kWh lithium-ion batteries would use up to 30% of the world’s known reserves of lithium. But lithium is also found in unlimited quantities in sea water^{3,4}, and concentrating it from brines is much greener (requiring just solar energy) than conventional mining. The demand for lithium could also be eased by recycling, which has already proved its value with lead–acid

batteries. All these problems must be overcome if lithium batteries are to take their place as the batteries of the future (Fig. 2).

The nanotechnology revolution

Most attempts to improve the design of lithium-ion batteries have tackled the problem at the macroscopic scale, but work is now focusing on the nanoscale. Nanomaterials were slow to enter the field of energy storage because the effective increase in the electrodes’ surface area raised the risk of secondary reactions involving electrolyte decomposition. Only as recently as 2000 was it realized that such reactions could be controlled by coating the electrodes to protect the electrolyte from unwanted oxidation or reduction by the electrode materials. The arrival of nanomaterials gave lithium-ion batteries a new lease of life⁶ and provided benefits in terms of capacity, power, cost and materials sustainability that are still far from being fully exploited.

Electrode kinetic issues can be circumvented by switching to nanomaterials combined with carbon ‘nano-painting’⁷, in which the grains are coated with a thin layer of carbon to bring the required conductivity to individual grains, whose small size shortens the diffusion path for ions and electrons. Moreover, by accommodating the strains associated with lithium insertion/removal reactions, as the volume can expand or contract several-fold, this has also made it possible to use materials with large volume changes on reaction with lithium, such as alloys. But there are pitfalls, the most important being the poor packing density of electrodes based on nanomaterials, which limits

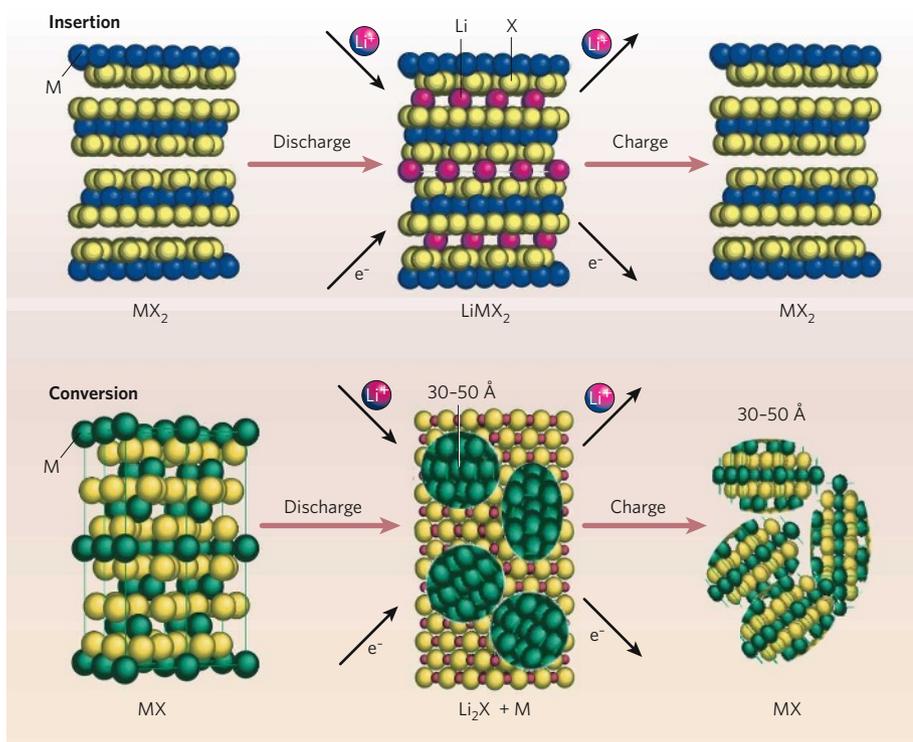
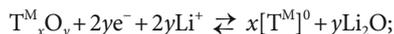


Figure 3 | Reaction mechanisms. Schematic representation showing the contrasting reaction mechanisms occurring during discharge for insertion (top) and conversion reactions (bottom). The insertion reaction demonstrates a maximum of 1 electron transfer per transition metal (here designated M), whereas the conversion reaction can transfer 2 to 6 electrons (derived from ref. 28).

the energy that can be stored per unit volume or mass because there is a larger proportion of ‘inert’ components such as current collectors or electrolyte.

Another advantage of nanomaterials is that they can change the reaction pathway, affording high capacities, rechargeability and generality to a range of battery systems⁸. One such reaction pathway is referred to as a ‘conversion’ from transition-metal oxides:



the final product consists of a homogeneous distribution of metal nanoparticles ($[T^M]^0$, where the superscript 0 indicates the metallic form) embedded in a Li_2O matrix (Fig. 3). The drawback with this mechanism, however, is that the large voltage difference between charge and discharge results in poor energy efficiency. This problem is being addressed by studies of both the material chemistry and morphology and the electrode configuration. The hunt is also under way for materials that can undergo conversion reactions involving multiple electrons at high potential, for use as cathode materials. However, the full impact of nanomaterials on living cells has yet to be appraised, although the risk is minimal when they are produced *in situ*, as they are for the conversion reaction.

Solid electrolytes were quicker to benefit from the use of nanomaterials⁹. The addition of ‘nano-fillers’ (nano-grains dispersed in a polymer, such as Al_2O_3 or TiO_2) to simple

polyether-based electrolytes increases the conductivity several-fold at 60–80 °C, but there is no advantage at room temperature. Organizing the polymer strands in such a way as to increase the order locally (using crystalline whorls, stretching or even chirality) can also provide benefits, by increasing conductivity at low temperatures, and further work is needed to assess the merits of using block co-polymers (AB or ABA)¹⁰. The phase separation inherent to these systems results in good mechanical properties, but also offers a way of increasing dissociation by partitioning anions and cations in the two sub-phases. Giving the two phases different wetting or adhesion properties can help by avoiding grain growth as the polymer’s nano-domains will determine the partitioning of space.

True polymer batteries may still be some way off, but in the meantime we will see more attempts to use ionic liquids as either solvents for lithium salts or plasticizers for polyether-based electrolytes. Ionic liquids have exceedingly low vapour pressures, are non-flammable and have high conductivities, making them serious contenders for safer batteries. But it remains to be seen whether they can be produced cheaply enough, at the desired purity, with sufficient conductivity at low temperature.

Beyond nanomaterials

The components of today’s lithium-ion batteries, such as $LiCoO_2$ and $LiMn_2O_4$, are not produced from renewable energy resources but from ores, and extracting the raw materials

and manufacturing the electrodes will require increasing amounts of energy as they become scarcer. Will the lithium-ion battery, which is so energetically expensive to fabricate, remain attractive and viable in the long term? In 50 years, if all cars become electric and rely on these scarce materials, might we face staggering price increases like those recently seen with fossil fuels? Not if we find a way of making lithium-ion batteries sustainable while maintaining or exceeding the performance of today’s batteries. One option is to use renewable electrodes made from natural resources, just as fuel cells can use hydrogen or (m)ethanol made from biomass. But what would these electrodes be like?

Inspired by nature

When scientists need new approaches, they often turn to the chemistry of life, with its virtually unlimited and incredible reaction mechanisms. The battery’s insertion reaction may have no real equivalent in the living world, but the materials themselves could be fabricated in living cells. Phosphate species are manipulated to make DNA and ATP, so it is not so hard to envisage an enzyme-mediated synthesis of $LiFePO_4$, especially as the pH for the precipitation is close to the physiological value of 7. The same outlook applies to conversion reactions, as preliminary work¹¹ has demonstrated the synthesis of hydrated Co_3O_4 and MnO_2 with the help of a virus and a bacterium, respectively.

Perhaps the ultimate in conversion reactions also comes from living systems. The protein apoferritin, which encloses a small crystal of iron oxide ($Fe_2O_3 \cdot nH_2O$), can either grow or dissolve the particle according to the organism’s current need for iron¹². So could polymers with properties rather similar to proteins, adsorbed on the surface of a conversion electrode, control the growth or dissolution of the $T^M_xO_y$ and Li_2O crystals, the reversible formation of which is key to increasing the energy efficiency?

Regarding the feasibility of using electrochemically active organic molecules as cathode materials, the use of polyaniline¹³ and other redox polymers¹⁴ has been much hyped over the years, but development has been disappointing. However, because lithium-exchanging materials do not involve the electrolyte in their redox processes, substituting the cathode for an organic material might boost the capacity. The feasibility of using active $Li_xC_6O_6$ organic molecules that can be prepared from natural sugars common in living systems (Fig. 4) is currently under investigation¹⁵. In the light of such findings, we can speculate on the use of hypericine (a polyquinone-based active ingredient of St John’s wort) or the condensation polymers of malic acid as potential high-capacity cathode materials.

The close relationship between carbohydrates and their oxidized polyketone forms makes the former the logical starting point for the design of new electrode materials.

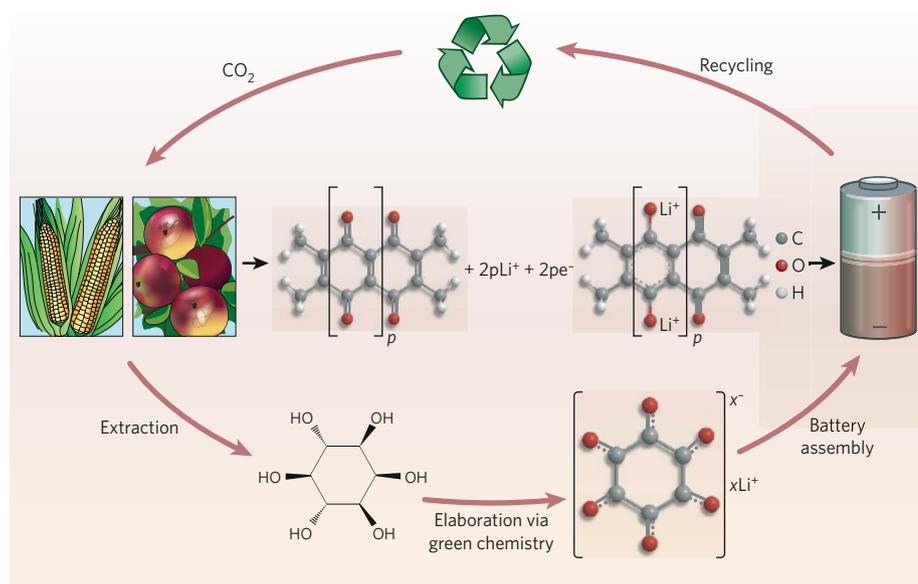


Figure 4 | An organic future. Proposed sustainable organic-based batteries based on electrode materials made from biomass. Myo-inositol extracted from corn can be used to prepare electrochemically active $\text{Li}_2\text{C}_6\text{O}_6$, whereas malic acid from apples can undergo polycondensation to a polyquinone that is electrochemically active to lithium (centre). (Derived from ref. 15.)

Polyketones can be obtained from natural sources and are unlimited because sugars can be made by living species or artificially in green chemistry¹⁶. Nor have sugars been overlooked for use in bio fuel-cells, a much improved version of which has recently been unveiled¹⁷.

Although complex and unlikely to yield instant results, the search for electroactive organic molecules synthesized from biomass could pave the way for the next generation of lithium-based batteries. Organic materials have already made considerable inroads into the semiconducting industry, in light-emitting diodes, solar cells and transistors, and they are expected to penetrate the energy field in the coming decades. However, it would be foolish to ignore the fact that organic materials have several disadvantages in terms of their limited thermal stability, low specific gravity and appreciable solubility in electrolytes.

Lithium-oxygen batteries

Air electrodes and metal-air battery technologies have already been used in primary systems such as fuel cells, but the use of lithium instead of zinc as the metal will increase the energy output eightfold. An oxygen electrode proceeding in tandem with lithium according to the reaction $2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2$ can deliver a capacity of $1,200 \text{ mAh g}^{-1}$. The first lithium-air cell was successfully assembled and discharged in 1996 (ref. 18), but attractive rechargeability was demonstrated only recently¹⁹.

It could be argued that such a system unites within the same device the two most prominent failures of battery and fuel-cell technologies, namely the inability to master lithium and oxygen electrodes. These perceived issues have prevented the practical use of lithium-air batteries. However, one advantage of such a system is the formation of Li_2O_2 without cleaving

the O–O bond, which has limited both kinetics and rechargeability in aqueous systems because there is a large activation energy and platinum catalysts are often required.

Improving energy storage and preventing Li_2O_2 from clogging the electrode require a better understanding of the reaction mechanism of the oxygen electrode. Engineering and chemical advances are also required to prevent the ingress of either CO_2 or H_2O , which could react with either Li_2O_2 or lithium metal. But there are reasons for optimism. The use of nanomaterials makes it possible to design porous, catalysed, three-dimensional electrodes²⁰ (Fig. 5) with improved kinetics and

energy efficiency. The use of ionic liquids, which can be made hydrophobic, will put an end to problems caused by the entry of water. However, if ionic liquids are to be used as electrolytes, they must be combined with a highly hygroscopic Li salt, so preparing them remains a serious challenge.

Lithium has been the anode of choice for years, but much more work is still needed. When used with liquid electrolytes and gels, the metal is redeposited unevenly in the form of dendrites, leading to inherently unsafe cells with a short lifetime. It has been suggested that the cause lies in current inhomogeneities induced by the passivation layer present on the surface of lithium metal²¹. Using dry polymer electrolytes instead keeps the problem at bay for the first 600 cycles, but does not solve it. The classic strategy²² to get uniform microcrystalline metal deposition in an aqueous solution from anionic complexes (for example, silver metal from $\text{Ag}(\text{CN})_2^-$) has not been applied to the lithium electrode. In this strategy, the surges in local current result in a drift of the negative ions from the interface, leading to a depletion of the plating species and hindering the formation of metal dendrites. The same principle could be applied to lithium systems by using charged chelating complexes of the LiX_2^- type, formed, for instance, using bidentate ligands of the 1,3-dione family (acetylacetonate) and having K^+ as a counter-cation (see Fig. 6).

Another approach would be to use unipolar electrolytes, in which only the cations carry charge, but these have never been seriously studied in the context of plating lithium metal. This is surprising because polyelectrolytes with fixed negative charges attached to a macromolecule are the only way to avoid the depletion or over-concentration of salt arising from the

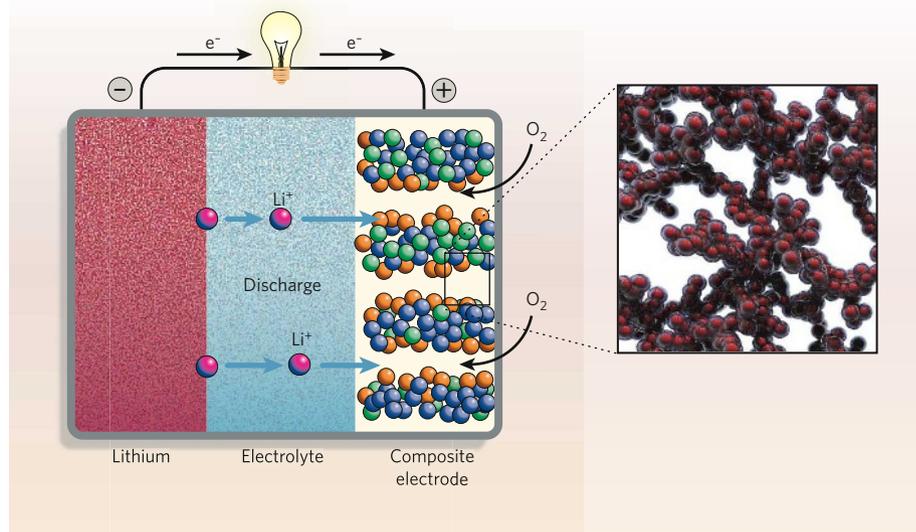


Figure 5 | Lithium-air batteries. Left, the mechanism used in lithium-air batteries (courtesy of A. Debard *et al.*, Univ. St Andrews). Right, three-dimensional nanostructured electrodes made from depositing 10- to 20-nm-thick layers of MnO_2 onto a carbon foam using a low-temperature process (according to ref. 20) that could be used to enhance the kinetics of the lithium-air electrode (three-dimensional schematic courtesy of J. W. Long and D. R. Rolison, US Naval Research Lab.).

Table 1 | Battery chemistries

Battery type	Features	Environmental impact
Ni-MH (established)	Low voltage, moderate energy density, high power density Applications: portable, large-scale	Nickel not green (difficult extraction/unsustainable), toxic. Not rare but limited Recyclable
Lead-acid (established)	Poor energy density, moderate power rate, low cost Applications: large-scale, start-up power, stationary	High-temperature cyclability limited Lead is toxic but recycling is efficient to 95%
Lithium ion (established)	High energy density, power rate, cycle life, costly Applications: portable, possibly large-scale	Depletable elements (cobalt) in most applications; replacements manganese and iron are green (abundant and sustainable) Lithium chemistry relatively green (abundant but the chemistry needs to be improved) Recycling feasible but at an extra energy cost
Zinc-air (established)	Medium energy density, high power density Applications: large-scale	Mostly primary or mechanically rechargeable Zinc smelting not green, especially if primary Easily recyclable
Lithium-organic (future)	High capacity and energy density but limited power rate. Technology amenable to a low cost Applications: medium- and large-scale, with the exception of power tools	Rechargeable Excellent carbon footprint Renewable electrodes Easy recycling
Lithium-air (future)	High energy density but poor energy efficiency and rate capability Technology amenable to a low cost Applications: large-scale, preferably stationary	Rechargeability to be proven Excellent carbon footprint Renewable electrodes Easy recycling
Magnesium-sulphur (future)	Predicted: high energy density, power density unknown, cycle life unknown	Magnesium and sulphur are green Recyclable Small carbon footprint
Al-CF _x (future)	Predicted: moderate energy density, power density unknown	Aluminium and fluorine are green but industries are not Recyclable
Proton battery (future)	Predicted: all organic, low voltage, moderate energy density, power density unknown	Green, biodegradable

mobility of the anions. These two strategies (anionic lithium salts and unipolar conductivity) should be further explored to ensure that all avenues towards making the lithium-metal electrode viable have been exhausted.

Alternatives to lithium

Although we have focused on lithium, there are several alternatives for use as electrodes (Table 1). The metals worth considering are magnesium (ref. 23) and aluminium (ref. 24) because of their light weight, but they deliver less voltage, undermining their use as anodes, and repetitive plating of these metals is difficult using most electrolytes. Similarly, only high-capacity cathode materials can be considered, which narrows it down to oxygen or sulphur for magnesium, or graphite fluoride for aluminium, to harness the metal's high affinity for fluorine. However, little is known about the kinetics of electrode reactions involving the motion of multivalent species, and addressing these challenges would need extensive collaboration between organometal researchers and electrochemists.

Proton-based battery technologies have been well studied, but do they still have anything to offer? Even with the best air electrode, to be competitive with lithium-ion batteries, a hydrogen system, with a voltage of 1.0–1.5 V, requires the anode to have an extremely low equivalent mass, far below that of conventional

hydrogen-storing alloys. The only candidates are light elements, given that C–H bonds are too covalent and cannot (yet) be activated for reversible room-temperature systems. Another alternative for the negative electrode would be to exploit the reversibility of the N–H bond in semiconjugated polymers (see Fig. 6). These low-potential (V versus H_2/H^+) materials could be used as high-capacity electrodes, although their low electronic conductivity could prove problematic.

Miniature powerhouses

As well as large-scale applications, such as electric vehicles, batteries must also be developed

to satisfy recent advances in microelectronics. These require miniature power sources, such as solid-state, lithium-based, thin-film batteries. Much of the work has focused on flat, two-dimensional configurations, but these are limited in terms of energy output, and the need for greater performance has recently led microbattery researchers to explore the third dimension²⁵. This might seem relatively easy, given the spectacular three-dimensional circuitry that the silicon microelectronic industry now has to offer. However, microlithography processes have proved both awkward and costly to transfer to batteries.

A combined chemical–electrochemical approach has much to offer as a way of manipulating materials at the atomic scale, and could be used to develop 'skyscraper' batteries (Fig. 7). Similarly, adding a third dimension opens the way to a larger variety of configurations (such as the assembly of positive–negative electrodes and electrolyte) while maintaining a short diffusion length for electrodes and ions, which is essential if a battery is to have the required power.

Conclusions

It is not yet clear whether the next generation of batteries could be successfully integrated into an energy market that is currently linked to global warming. Fame and fortune certainly await anyone who can come up with a viable alternative to fossil fuels. Furthermore, it is difficult to see how the performance gap between the internal-combustion engine and lithium-ion batteries will be filled using only new battery technology; other approaches, such as fuel cells, will be needed, but here a complete overhaul of present systems will probably be required.

In our journey into the future we have reinvestigated existing systems and suggested new trends and ideas that require much work to become a reality. Designing green and sustainable battery systems is essential, so criteria such as life cycle, abundance of raw materials and electrode recycling are becoming crucial. For these reasons, much is expected of the lithium–air system, which offers a great improvement in energy density, and lithium-

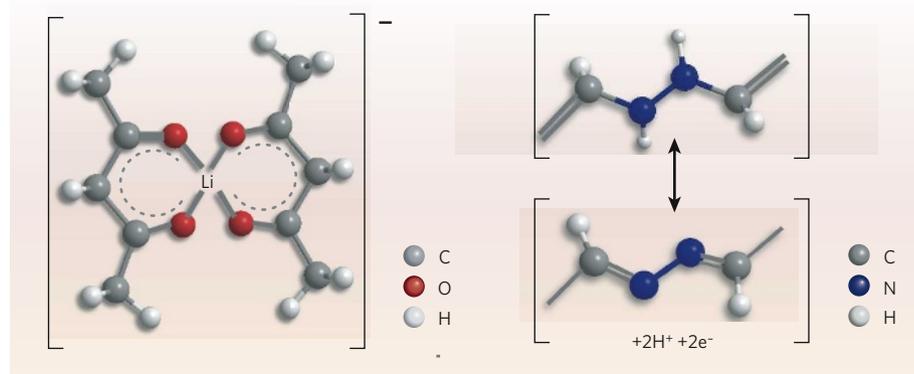


Figure 6 | Wild cards. Lithium-bearing anionic complexes that could be explored for efficient lithium plating (left) and a contender for a high-capacity proton-exchanging polymer (right).

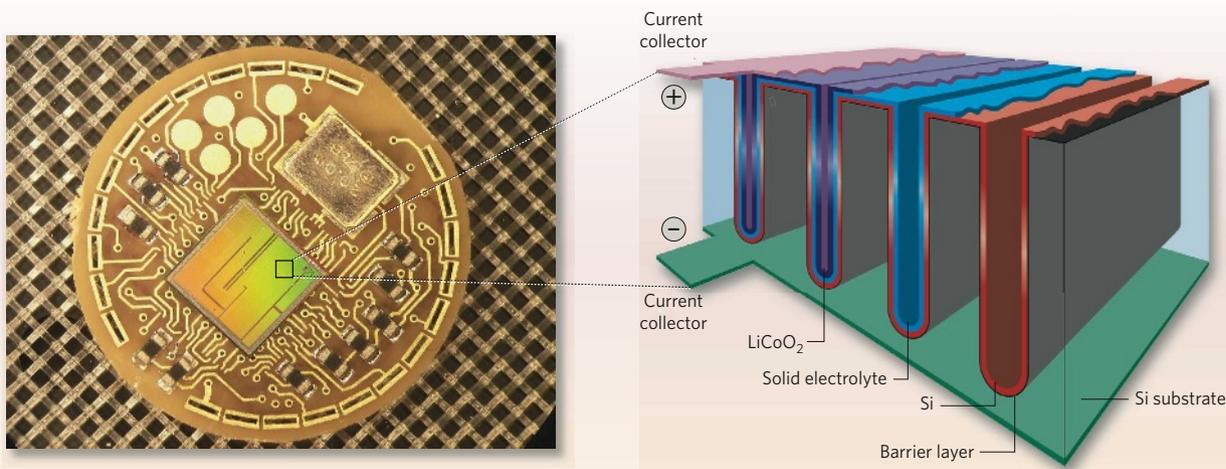


Figure 7 | Entering the third dimension. Schematic representation of a three-dimensional, integrated, solid-state lithium-ion battery. The surface area of the battery has increased 25-fold compared with a two-dimensional thin-film battery with the same footprint surface area, and will therefore be

able to provide enough energy to power smart autonomous network devices related to sensing applications. (Courtesy of P. H. L. Notten, R. A. H. Niessen and L. Baggetto, Philips Research Laboratories, and Technical University of Eindhoven, the Netherlands.)

based systems that use electroactive organic molecules, which could be obtained from biomass using green chemistry. Yet it seems incongruous to insist that batteries are sustainable while the car or appliance they drive is not.

The next generation of lithium-ion batteries fully based on nanomaterials will soon be here, followed by lithium-air batteries and others using organic materials. And there is plenty to inspire us in the living world, as long as we can capture the function of each molecule in a cumulative sequential process, which is not an easy task. Both biofuel cells and high-voltage liquid-electrolyte microbatteries inspired by electric eels have already been demonstrated. We all live on organic-based energy, so why shouldn't our appliances and vehicles use it too?

One thing is clear, however. Solving the remaining challenges will require researchers from a range of disciplines, and their success will depend on the efficiency of their cross-fertilization. ■

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Acknowledgements The authors wish to thank the scientific community in the field of energy storage and conversion for laying the foundations for these views. They are also grateful to G. Amatucci, D. Murphy and P. Poizat for valuable comments.