REVIEW

Key challenges in future Li-battery research

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Batteries are a major technological challenge in this new century as they are a key method to make more efficient use of energy. Although today’s Li-ion technology has conquered the portable electronic markets and is still improving, it falls short of meeting the demands dictated by the powering of both hybrid electric vehicles and electric vehicles or by the storage of renewable energies (wind, solar). There is room for optimism as long as we pursue paradigm shifts while keeping in mind the concept of materials sustainability. Some of these concepts, relying on new ways to prepare electrode materials via eco-efficient processes, on the use of organic rather than inorganic materials or new chemistries will be discussed. Achieving these concepts will require the inputs of multiple disciplines.

Keywords: cells, batteries; energy

1. Introduction

Energy is the lifeblood of modern society. Global warming, finite fossil-fuel supplies and city pollution conspire to make the use of renewable energy, together with electric transportation, a worldwide imperative. There is a pressing need to design electrical-energy-storage systems to balance supply with demands, as renewable sources are intermittent, and to power the upcoming plug-in hybrid electric vehicles (PHEVs) or electric vehicles (EVs). Numerous energy-storage solutions enlisting mechanical, magnetic, chemical storage, etc., are being presently investigated. Therefore, as we want to store energy in order to restore it as electricity, the most attractive path is to convert chemical energy into electrical energy, as they both share a common carrier, namely the electron. Fuel cells and batteries are electrochemical storage devices that ensure such conversions to occur in a single or reversible way, respectively. As fuel cells are frequently referred to as an emerging technology, in spite of 200 years of research, we have focused this paper on batteries since they are the main contenders to better manage the renewable resources of our planet, and to favour the

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deployment of electric cars so as to limit pollution. It should indeed be recalled that each time we burn 1 litre of gasoline, we are liberating 1.5 kg (e.g. 750 l) of CO₂.

Among present battery technologies, Li-ion technology is the best performing one owing to its delivered energy density (210 Wh kg⁻¹; 650 Wh l⁻¹), which exceeds any competing technologies by at least a factor of 2.5 (Tarascon & Armand 2001). With such attractive performances, coupled with its long life cycle and rate capability, Li-ion technology has captured the portable electronic market, invaded the power tool equipment market, previously kept for Ni–MH technology, and is on the verge of penetrating the EV market on condition that improvements can be achieved in terms of cost and safety. Indeed, long-term stability, high-energy density, safety and low cost seem to be the over-riding factors in high-volume applications. Therefore, it implies assessing present Li-ion technology so as to define the challenges that lie ahead to ensure its long-lasting success (Armand & Tarascon 2008). Attempts to answer such questions will constitute the core of this paper, which will mainly, but not exclusively, deal with Li-ion technology. Research directions to increase the Li-ion battery energy density, lower its cost, improve its safety and make it more sustainable and ‘greener’ will be discussed. New upcoming chemistries will also be brought to the scene and benchmarked with today’s systems.

(a) Means to increase energy density

Despite the new lease of life recently brought by the arrival of nanomaterials, present Li-ion technology falls short of meeting all of the requirements dictated by the large volume of applications linked to renewable energy and electric transportation fields. First, we should be aware that a colossal task is awaiting us if we really want to compete with gasoline, as an increase by a factor of 15 is needed for the energy delivered by a battery (180 Wh kg⁻¹) to match the one of a litre of gasoline (3000 Wh l⁻¹; taking into account corrections from Carnot’s principle). Knowing that the energy density of batteries has only increased by a factor of five over the last two centuries, our chances to have a 10-fold increase over the next few years are very slim, with the exception of unexpected research breakthroughs. Fortunately, the automotive industry has set a more realistic target: doubling the present Li-ion energy density in the next 10 years so that the autonomy of EVs approaches 500 km. The energy density of a battery is the product of its capacity and its potential, and is mainly governed by the capacity of the positive electrode. Simple calculations show that an increase in cell energy density of 57 per cent can be achieved by doubling the capacity of the positive electrode, while one needs to increase the capacity of the negative electrode by a factor of 10 to get an overall cell energy density increase of 47 per cent (Tarascon 2002). So, the chances of drastically improving today’s Li-ion cells energy density are mainly rooted in spotting better positive electrode materials, i.e. materials that could either display greater redox potentials (e.g. highly oxidizing) or larger capacity (materials capable of reversibly inserting more than one electron per 3d metal).

Knowing that the redox potential of an intercalation compound mainly tracks the iono-covalency of the metal–X bonding, fluorine (F) substitution appears to be quite an attractive direction to increase the material redox voltage (V), as F
is very electronegative. Therefore, a drawback brought about by F substitution concerns materials having large band gaps (e.g. poor electronic conductivity), which usually display poor ionic conductivity when containing Li. As the latter is an intrinsic value, there is a need to synthesize these materials at the nanoscale, as the intercalation time (e.g. the time for Li ions to move from the core to the particle surface) decreases with the square root of the particle size. These nanoparticles must additionally be carbon coated if one ever wants these F-based materials to be competitive in terms of power-rating capabilities. Apart from fuelling electrons through the entire electrodes, carbon coatings, which stand as a buffer layer between the active material and the electrolyte, also help in minimizing electrolyte degradation; the latter is usually quite important, with highly oxidizing electrode materials functioning at potentials well beyond the thermodynamic potential of the electrolyte (Simon & Tarascon 2009).

Another approach towards increasing energy density consists of identifying materials that could reversibly accept more than one electron per 3d metal. At first sight, Li₂MnSiO₄ appears quite attractive, as the presence of Mn²⁺ could imply the feasibility of removing two lithium atoms (Mn²⁺ → Mn⁴⁺ + 2e⁻). So far, experimental attempts (Gong et al. 2006) have remained unsuccessful in accordance with theoretical calculations (Gaberscek et al. 2007; Kokalj et al. 2007), which indicate the non-thermodynamic stability of the fully delithiated MnSiO₄ phase. This further confirms the difficulty in spotting compounds that
could reversibly react with lithium via an insertion/de-insertion process involving more than one Li\(^+\) per 3d metal. This contrasts with conversion reactions that can enlist, according to the overall reaction \((M_nX_y + \ldots)\), the reversible uptake of two (CoO) \((\text{Poizot et al. 2000})\) to six Li\(^+\) (NiP\(_2\)) \((\text{Gillon et al. 2005})\) per 3d transition metal at potentials that depend on the iconicity of the M–X bond, with the highest redox potential for the highest electronegative anion (e.g. F\(^-\)). However, the main drawback in the conversion of positive electrodes (FeF\(_3\)) lies both in their high polarization and in the absence of Li in their initial stage, so that they can only be used in Li rather than Li-ion cells. To eschew the latter, there is always the feasibility of making (MX–LiX) composites via ball-milling, which can be used as a Li reservoir and be stable in a moisture environment if the conversion redox potential exceeds 3.2 V \((\text{Amatucci \\& Pereira 2007})\) burning 1 litre. In contrast, chances of lowering the polarization for conversion electrodes remain slim since we have shown that this polarization is linked to the iconicity of the M–X bond and its redox potential, both increasing with compounds showing a high ionic character (fluorides) and decreasing with highly covalent compounds (hydrides) \((\text{Oummellal et al. 2008})\). However, owing to the staggering capacity gain that such electrodes provide, they should continue to be a high-topic research, even though the remaining task of increasing their energy efficiency is not perceived as an easy one.

Interestingly, most of the new paths mentioned to increase energy density result in the use of materials whose both electronic and ionic properties are very poor; therefore, the need to grow highly divided materials in order to decrease the Li-ion transfer path for Li uptake/removal is a must, as well as the use of conductive coatings for providing electrons throughout the entire electrode \((\text{Arco et al. 2005})\). Carbon coatings combined with particle-size reduction have been successfully used to trigger the electroactivity of LiFePO\(_4\) \((\text{Ravet et al. 1999})\).

Although quite useful, such an approach cannot be used for highly oxidizing compounds such as LiCoO\(_2\) and LiFePO\(_4\)F, for instance, because of the reducing nature of the carbon treatment, which results in decomposition of the treated material; hence, the need to find alternatives to improve electrode kinetics \((\text{Gaberseck et al. 2005; Gaberseck \\& Jamnik 2006})\). With all the limitations that such a comparison could bear, an electrode material can be visualized as our brain, where all the neurones (in our case active nanoparticles) must be electronically and ionically nicely wired to ensure proper functioning. Mindful of these considerations, several approaches, most of which consist of controlling electrode architecture at the nanolevel, have been pursued (figure 1). They enlist the design of electrodes based on molecular bridging via the coating of particles with electron-conducting polymers such as polyethylene di-oxyethylene thiphene (PEDOT; \text{Meng et al. 2003; Shen \\& Lee 2005}), or the grafting of a molecular conductor redox relay (e.g. 3.5 V versus Li/Li\(^+\)) such as triaryl amine substituted for a benzyl phosphonate group, as recently demonstrated by Greatzel’s group on LiFePO\(_4\) \((\text{Wang et al. 2007})\). Parallel approaches consisting of (i) preparing highly mixed solid conductor composites (e.g. CuF\(_2\)–MoO\(_3\)), as demonstrated by Amatucci’s group \((\text{Badway et al. 2007})\) and (ii) growing ordered mesoporous materials \((\text{Bruce et al. 2008})\), consisting of micrometre-sized particles, within which pores of 2–5 nm do exist to host the electrolyte, have been successfully made. For such concepts to fully reach fruition, there are some remaining challenges. While the approach referred to as either inverse structuring, replica or
chemical templating, has been successful in preparing numerous binary phases, it has been solely limited to LiMn$_2$O$_4$ for Li-bearing positive electrodes (Bruce et al. 2008). Hence the need to grow ordered mesoporous Li-bearing positive electrodes if one wants such a new class of poorly conducting electrodes (silicates, phosphates and fluorophosphates) to be efficiently implemented in Li-ion cells. Additionally, further studies must focus on the molecular-bridging approach, with the need to (i) design, on demand of molecular layer, relays having a redox potential closely matching that of the insertion material, (ii) search for electron-conducting polymers beyond PEDOT, together with better chemical means to ensure a uniform coating, and (iii) identify mixed ion/electron-conducting polymers. Although this last task may appear tremendous, the pay-off could be huge, as mastering electrode wiring is keen in the optimum functioning of electrochemical storage devices, regardless of what they are (supercapacitors, batteries, fuel cells, etc.).

(b) Means of increasing safety

Manipulating energy inevitably leads to intrinsic safety risks that hold regardless of the devices or electrochemical systems used, with the rule of thumb being that the risks increase with the size of the energy-storing device; hence the requirement for extra safety conditions for large-sized batteries in the case of PHEV and EV applications. Numerous attractive solutions relying on either the use of chemical additives to the battery electrolyte (solid–electrolyte interface (SEI) modifiers, shut-down and redox shuttles additives, ionic liquids) or improved cell design and electronics have been pursued, as shown in figure 2; therefore, Li-ion technology is not exempt from incidents. More conservative approaches (Ariyoshi & Ohzuku 2007) consist of coupling a highly oxidizing positive electrode material (LiMn$_2$O$_4$ or others) with a less reducing material (Li$_4$Ti$_5$O$_{12}$ instead of carbon) in order to eliminate the formation of a solid electrolyte interface at the negative electrode, which is a source of concern when dealing with safety. Therefore, this approach provides extra safety at the expense of the battery performance, as LiMn$_2$O$_4$/Li$_4$Ti$_5$O$_{12}$ Li-ion cells display a low energy density of 85 Wh kg$^{-1}$ when compared with 140 Wh kg$^{-1}$ for LiMn$_2$O$_4$/C cells (Amezutsumi et al. 2007). Overall, it turns out that whatever the followed approach might be, safety and cost follow each other. Along that line, it is unfortunate that, today, the Li-ion battery is the victim of fierce cost cutting and attempts to cram more and more energy in the same volume; therefore, there is a constant risk of safety issues.

Besides accepting this cost–safety tie, future Li-ion technology will undoubtedly rely on a sound understanding of electrode–electrolyte components, especially as we move to the next generation of either positive electrodes based on higher voltage (5 V) insertion nanomaterials or negative non-insertion electrodes (e.g. Li-alloying or conversion reactions) made of highly divided materials. Novel strategies to harmoniously couple the next generation of cathodes or anodes with suitable electrolytes will have to be found. Future research necessitates to challenge past basic understanding of electrode–electrolyte interfaces, designing new cell components (electrodes, electrolytes, additives), and also setting up new experimental protocols to better analyse the electrolyte degradation products in either a passive (in situ) or active (post-mortem) way.

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Figure 2. Safety aspects in Li batteries. The various chemical and engineering/devices approaches aimed towards increasing Li-ion battery safety are mentioned. Distinction is made as a function of both (i) the type of applications considered (y-axis) and (ii) the type of redox chemistry involved (x-axis). Designing low-voltage systems, Li₄Ti₅O₁₂/LiFePO₄, increases safety at the expense of cost, conveying the general message that changes in safety and cost always track each other. While long far-reaching, the development of solid-state batteries is mentioned as the ultimate solution to reach zero risk. (Adapted from ALISTORE-ERI white paper on safety; M. Armand, P. G. Bruce, L. Croguennec, M. Morcrette & J.-M. Tarascon 2008, internal communication.)

The use of solid-state Li-ion batteries based on either dry polymer or inorganic electrolytes can be seen as the ideal solution. More than 30 years of research has already taken place in this research field, but several hurdles do still remain. For such an idealistic situation to come through, drastic improvements and breakthroughs must occur so as to increase the electrolyte conductivity. With the present renewed interest in both room- and high-temperature solid-state batteries, together with the new records achieved in glass-ceramic conductivities ($10^{-3} \text{S cm}^{-2}$) within the Li$_2$S–P$_2$S$_5$ system (Minami et al. 2007), or LiBH$_4$–LiI (Maekawa et al. 2009), together with new electrode-assembly techniques, optimism must prevail. Within the field of dry-polymer research, our challenge nowadays is to end 30 years of frustration with an approach to design better ion-conducting polymers to enable the 25°C operating temperature. A colossal amount of work went into the exercise of loading polymeric matrices with nano-inorganic fillers (Croce et al. 1998); but, the results still fall short of meeting expectations. Aware of the positive attributes of nanostructuration to the cell electrode components, time has certainly come to implement the same concepts to the design of future polymer electrolytes. Although the nanostructuration of polymers has remained rather neglected, it is believed that approaches relying
Figure 3. Towards energy and materials thrift for LiFePO₄ preparation. Numerous methods enabling both a lowering of the synthesis temperature and the formation of highly divided powders. While ceramic, hydrothermal and solvothermal approaches are well established, the ionothermal synthesis approach is totally new. The biomineralization approaches are well known, but their in-road within the field of electrode materials synthesis is just appearing (Tarascon et al. 2010).

on nanophase separation in block copolymers or self-organization of polar and non-polar bloc copolymers at the nanoscale could have a bright future based on the design of high ion-conducting polymer membranes.

(c) Means of reducing costs

There are numerous means of enlisting both engineering (cell manufacturing and assembly) and chemical (materials design and electrode composition) factors to combat the exceedingly high cost of the Li-ion technology, which nowadays ranges from 800 to 300 $kWh^{-1}$, as opposed to about 50–100 $kWh^{-1}$ for lead-acid technology. At the material level, which is the focus of the paper, the cost is mainly dependent upon the material-synthesis process, its abundance and renewability. This is the reason why materials based on sustainable 3d metal redox elements such as Mn (LiMn₂O₄), Fe (LiFePO₄, Li₂FeSiO₄) and even Ti (TiO₂, Li₄Ti₅O₁₂), and made via eco-efficient processes, are receiving increased interest with respect to Co or Ni-based electrodes relying on limited elements, and which are usually made at high temperatures. Nevertheless, although LiFePO₄ is a mineral known as ‘triphylite’ in nature, it cannot be used directly as such owing to its poor conducting properties. Synthetic triphylite has to be made aiming at grain sizes that can be directly processed looking for the most expeditious and energy-saving processes (Recham et al. 2009a,b).

Aware of this conjuncture, chemists have greatly explored, over the last few years, new eco-efficient ways to process electrode materials (figure 3) by first revisiting classical hydrothermal (Chen et al. 2007)/solvothermal (Delacourt et al. 2006) synthesis paths, which mainly consist of reacting in water metal–non-metal-based soluble salts with a base, and increasing the temperature to promote the growth of the desired phase via Ostwald ripening. Besides the feasibility of proceeding at low temperatures (e.g. low energy demand) and in a water
medium (e.g. green solvent), such processes enable, via fine-tune control of the reaction pH, the concentration of the precursors, with the preparation of homodisperse powders having a well-defined shape and size. It contrasts with ceramic methods, which require high temperatures (e.g. high energy demand) to ensure the diffusion of the reactants and the growth of the grains, usually leading to highly polydisperse powders.

Other innovations brought back by revisiting low-temperature-synthesis methods enlist (i) the appearance of microwave-assisted solvothermal processes (Theivanayagam et al. 2008) that shorten reaction times and therefore stand as an attractive high-throughput synthesis method and (ii) the implementation of ionothermal synthesis to the field of inorganics with very appealing results (Recham et al. 2009a,b). Like water, ionic liquids provide a highly solvating and reacting medium while showing no volatility, so that the use of cumbersome autoclaves, needed when operating in water, is no longer necessary. Moreover, owing to the flexible chemical design of cationic–anionic pairs, they present, as solvents, great opportunities for purposely directing nucleation (Recham et al. 2009a,b). Using ionothermal synthesis, nanopowders of numerous known electrode materials (Recham et al. 2009a,b) were made in glass vessels at temperatures below 250°C, while temperatures greater than 600°C were necessary to make heterodisperse powders by the ceramic process. Ionic liquids are definitely costly; therefore, their initial cost is deemed by the fact that they can be recycled several times without any need for purification when preparing several batches of the same materials. This newly developed synthesis method is rapidly getting recognized worldwide by numerous groups. It offers great opportunities towards the stabilization of new materials and, as a high-throughput synthesis method, to rapidly map ternary phase diagrams. Therefore, it still requires some energy, as temperatures of 200–280°C are usually required.

When scientists have to find extreme eco-efficient synthesis processes, they often turn to life chemistry, which is rich with virtually unlimited and incredible reaction mechanisms. For more than millions of years, micro-organisms have learnt how to make nanostructured materials or hierarchical porous structures under ambient conditions. Mindful of these considerations, bioinspired or biomimetic approaches towards material sustainability and renewability issues are appealing, and we are witnessing increasing numbers of studies in the biomimetic field of electrode materials for Li-ion batteries (Tarascon 2008). Biologically induced mineralization via the use of a bacterium by the name of ‘Bacillus pasteurii’ has long been reported for calcite precipitation (Wang et al. 1999; Sondi & Matijevic 2001). Using the same bacterium to provoke the hydrolysis of urea and generate a basic medium, we recently witnessed some evidence for the possible growth of LiFePO4 nanofilaments at temperatures as low as 65°C (F. Guyot, N. Reham & J. M. Tarascon 2008, unpublished results). As spectacular, although not yet practical, is Belcher’s recent work (Lee et al. 2009) on the use of engineered viruses as templates to make, at room temperature, high-rate FePO4/single-walled carbon nanotube electrodes. Biological principles will be, in the years to come, more intensely implemented in the rational design and assembly of battery components, and this is a good thing that we must pursue.

All the abovementioned systems are Li based, and we cannot remain insensitive to the controversial debates about Li resources and more so regarding low-cost ones. Today’s lithium comes from brines, mainly located in Chile and Bolivia.
(Meridian International Research 2006, 2008). Foreseen feedstock considerations already blow the whistle on Li resources, with the risk that they could not cope over the next decades with the increasing Li demands dictated by automotive transportation and grid-related applications. Alternatively, Li can be found in unlimited quantities in sea water; but, its recovery is more tricky and expensive than extracting it from brines via a concentrating step that just requires solar energy, as is done today. In anticipation of such a scenario, new chemistries must be envisioned, and the most appealing alternative relies on the use of Na instead of Li, as such an alkali metal is resource unlimited and easy to recuperate. Sodium has already been successfully implemented in today’s commercialized high-temperature Na/S cells for MW storage or Na/NiCl2 ZEBRA-type systems for EVs, both of which take advantage of highly conducting Na-β-alumina ceramics. Mindful of these considerations, the development of a room-temperature Na-ion cell should be feasible. At present, we do not see any obstacles to achieving Na-ion cells, as long as part of our research community is willing to deviate from the appealing Li-ion technology, and search for both positive and negative Na-insertion electrodes. Highly oxidizing positive Na-electrode materials (Na0.44Mn2O4; Na2FePO4F) (Ellis et al. 2007) capable of acting as a sodium reservoir do exist; in contrast, designing materials capable of inserting Na at a low potential remains to be an untouched field. It is then left to the solid-state chemist’s intuition, coupled with the theorist’s guidance to break new ground in this new research. It should therefore be put forward that Na-ion cells, which could use either liquid, ionic or solid electrolytes, will always fall short of meeting energy densities of the Li-ion counterparts, as Na is heavier than Li and is less reducing (e.g. lower potential). For large-volume applications, such drawbacks are overcompensated by the low cost of Na associated with its unlimited resources.

(d) Means to achieve sustainable and greener Li-ion batteries

Besides the aforementioned considerations of materials abundance and syntheses, which inflict a lower carbon footprint, the concept of renewable electrodes is becoming increasingly important and more so as battery recycling will become mandatory owing to the foreseeable mass production dictated by the EV market. The recycling of batteries from regular solid wastes is a thermal-recovery process that, in addition to raw-material extraction and electrode processing, adds further energy consumption to the battery life-cycling cost. To eschew such difficulties, an idealistic foreseeable view for battery processing in the years to come could consist (figure 4) of using electro-active organic electrode materials synthesized from ‘green chemistry’ concepts through low-cost processes free of toxic solvents; this will also enlist the use of natural organic sources (CO2 harvesting entities) as precursors, which will be biodegradable and easily destroyed by combustion (providing CO2), so that the battery assembly/recovery process will have a minimum CO2 footprint (Chen et al. 2008).

Going deeper into the notion of sustainability and renewable electrodes, our group recently explored the field of organics in the hope of unravelling organic molecules that show attractive electrochemical characteristics in terms of voltage and energy density. With respect to positive electrodes, we revisited the old chemistry of oxocarbons with special attention to the lithium rhodizonate (Li2C6O6) phase (Chen et al. 2008). Such a molecule, within which carbon
Figure 4. Schematic for battery assembling and recycling with zero carbon footprint. It enlists the use of natural precursors, which are easy to extract and which could be transformed into an electrochemical active electrode material via ‘green chemistry’. Later, upon recycling, the battery will liberate the CO₂ that will be used for further biomass production (courtesy of P. Poizot).

Atoms are bonded to carbonyl oxygen atoms, was found to present performances with a capacity of 540 mAh g⁻¹ greatly exceeding the one of today’s LiCoO₂ positive electrode (150 mAh g⁻¹). Besides, such an electrode has the advantage of being fully sustainable since it is made from the oxidation of a carbohydrate, named myoinositol, which can be made from natural products, more specifically from the disphosphorylation of phytic acid. At this juncture, let us recall that phytic acid is widely distributed in plants and accounts, for instance, for 8 per cent of the dry weight of corn-steeping liquor. Further screening for electroactive organic molecules versus Li⁺/Li⁰ showed molecules having carboxylate groups conjugated with the molecule core (Armand et al. 2009), such as lithium terephthalate (Li₂C₈H₄O₄); the latter shows a capacity (340 mAh g⁻¹) approaching that of the carbon negative electrode (372 mAh g⁻¹) presently used in Li-ion cells, while having safety advantages and an irreproachable environmental benefit, since it could be made by recycling the ubiquitous plastic polyethylene terephthalate. An Li-ion cell, based on fully renewable positive and negative organic electrodes, showing an acceptable level of performance, was recently assembled (Chen et al. 2009).

However, as usual with any new concept, they have their pitfalls, and this one is no exception. Besides the solubility issue associated with the use of single molecules rather than monomers or polymers, there is the need to isolate a multifunctional organic molecule whose Li salt could be oxidized while being air stable. Indeed, although Li₂C₆O₆ contains two Li⁺ ions, they cannot be electrochemically removed since, upon oxidation, the compound falls apart liberating, among others, CO₂ and forming carbonates. What is wanted are Li-bearing molecules capable of undergoing a reversible insertion–de-insertion reaction at a potential
Figure 5. The battery technology landscape as personally believed. For obvious reasons, the time scale is left open since bringing a new concept to commercial fruition bears some uncertainties. Even with an aggressive projection, whatever the type of technologies considered, we solely propose a two-fold increase in energy density over the next 30 years, and this will most likely come from the Li–air system. For applications from which cost and materials resources are crucial, organic Li ion and Na ion will play an important role in the years to come. It should therefore be stated that such predictions do not take into account complete out-of-the-box solutions to electrochemically store electricity, but some of the concepts related to the latter are hopefully maturing in a few laboratories.

exceeding 3.2 V. Organic electrodes have been criticized in the past for their poor performances, the reason why they fell into oblivion. Therefore, owing to their renewable aspects, combined with their performances amenable to those of the present Li-ion electrodes, we view them as the most wanted electrodes in years to come to make Li-ion batteries with no carbon footprint.

(e) Means of increasing capacity while ensuring sustainability and green storage

The renewable aspect brought out by organic electrodes nicely secures Li-ion technology in terms of sustainability and greenness. Performance-wise (gravimetric energy density, life cycle and power rate), such electrodes can easily be amenable to the performance of today’s best inorganic electrodes, but chances of outpacing them in terms of energy density are very slim. In the long term, improving the Li-ion technology while preserving its sustainable aspect will require out-of-the-box solutions. Metal–air systems (Zn–air, Al–air and more so Li–air) have long been recognized as great candidates for achieving staggering energy-density increases. However, despite the efforts that went into these technologies, very little progress has been made regarding their reversibility so that they rapidly fell into oblivion. Using the most attractive Li–air system as a reversible battery must at least clear three scientific/technological
hurdles: (i) designing efficient oxygen electrodes knowing that confectioning such electrodes has been a nightmare for fuel cells, (ii) ensuring the development of electrode formulations that are capable of solvating oxygen and are stable with respect to the superoxide anions, and (iii) mastering the Li–electrolyte interface that we could not solve for the last 25 years within the field of Li batteries, the reason why the presently successful Li-ion battery technology has surfaced in the first place. Solving all of these at once is a colossal task that will require several years of cooperative research. However, tremendous progress in developing Li-ion technology can be witnessed, and convincing data showing the possibility of achieving reversibility does exist (Debart et al. 2008). The oxygen electrode in an Li–air cell mainly consists of a carbon mat-supported catalyst, which serves as the host structure for the reversible formation of Li₂O₂ according to the following reaction: 2Li⁺ + 2e⁻ + O₂ → Li₂O₂. Mindful of the various approaches developed with the field of Li-ion batteries to design nanocomposites/nanoarchitected electrodes, together with rapid screening of new catalysts having special shape, structures and morphology, P. Bruce’s group (Debart et al. 2008) has succeeded in preparing electrodes that display for a few cycles (figure 4) reversible capacities as high as 1000 mAh g⁻¹, this corresponds to a six- to eight-fold increase when compared with today’s LiCoO₂ electrodes. However, prior to implementing Li–air-powered cars, a number of engineering and chemical challenges, such as improving the lifecycle of this electrode, together with its energy efficiency (e.g. reducing the 1 V upset between subsequent charges/discharges cycles), together with designing appropriate electrolytes and mastering the Li interface, have to be overcome. Optimism must therefore prevail owing to the increasing number of groups becoming involved with the Li–air system following Bruce’s pioneering work.

Another attractive system in terms of performances and sustainability, which has been around for more than two decades, is the Li–S system. Similar to the Li–air system, sulphur instead of oxygen is reduced at the positive electrode (S + 2Li⁺ + 2e⁻ → Li₂S) to produce solid Li₂S instead of solid Li₂O₂, with the difference that sulphur is solid and not gaseous like oxygen. Present Li–S cells show a better cycle life and greater efficiency (0.2–0.4 V between subsequent charge and discharge) than the Li–air ones, although their intrinsic energy density is lower. Their main drawback relies on the formation of soluble polysulphide (LiSnₓ) species during reduction leading, upon subsequent cycling, to a progressive detrimental capacity fade. To eschew such a difficulty, carbon mesoporous nanoarchitected electrodes, loaded with sulphur via an injection process, were successfully designed, showing better cycle life than any previously reported S electrodes (Ji et al. 2009). Overall, Li–air and Li–S technologies share the same problems, and this is beneficial, as any advance in Li–air can be directly implemented in Li–S and vice versa. Their penetration into the market is a few years ahead, with LiS most likely being the first one.

2. Conclusions

Batteries have been around for more than 200 years, and they are increasingly becoming part of our everyday life. Nevertheless, they are constantly criticized for their poor performances as they can never meet users’ unconditional demands.

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Thus, progress in battery research is frequently in the spotlight, as energy storage is far from following Moore’s law (doubling of the storage capacity in 18 months) that dictates memory storage. In spite of all this, we hope to have conveyed, through this article, the message that the landscape of battery energy research is rapidly changing worldwide. Researchers are leaving traditions behind and searching for new concepts embracing fundamental studies. The implementation of electrodes, enlisting raw abundant elements made via eco-efficient processes or obeying the renewable concept with zero carbon footprint, together with recent advances in sustainable and green Li–air systems, is shaping a bright future for electrochemical storage over the years to come. Although risky, we dared share, as personally perceived, our view of the battery landscape for the next decades (figure 5). Regardless of the fact that future predictions are very hard, it is a certainty that sustainable and greener Li-based storage technologies will no longer be science fiction in the years to come. Achieving such a next generation of storage technologies will eagerly require interdisciplinary approaches, and our success will depend on how good we are in setting cross-fertilization between these different disciplines.

Addressing energy-related issues is a worldwide problem shared by many countries. Nevertheless, while targeting similar objectives and having similar road maps, various countries have tendencies to favour national over worldwide programmes. Time is limited, and it is urgent for our politics to find means/infrastructures to enhance the cross sharing of information between national programmes dealing with energy-related matters, both at the European and international levels. Concrete actions must be rapidly taken if we want to secure a bright future for the generations to come and to our planet as a whole.

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