



Review

Lithium batteries: Status, prospects and future

Bruno Scrosati*, Jürgen Garche

Dipartimento di Chimica, Università di Roma "Sapienza", Piazzale Aldo Moro 5, 00185 Rome, Italy

ARTICLE INFO

Article history:

Received 4 September 2009

Received in revised form

12 November 2009

Accepted 12 November 2009

Available online 18 November 2009

Keywords:

Lithium batteries

New materials

Electrolyte

Anode

Cathode

ABSTRACT

Lithium batteries are characterized by high specific energy, high efficiency and long life. These unique properties have made lithium batteries the power sources of choice for the consumer electronics market with a production of the order of billions of units per year. These batteries are also expected to find a prominent role as ideal electrochemical storage systems in renewable energy plants, as well as power systems for sustainable vehicles, such as hybrid and electric vehicles. However, scaling up the lithium battery technology for these applications is still problematic since issues such as safety, costs, wide operational temperature and materials availability, are still to be resolved. This review focuses first on the present status of lithium battery technology, then on its near future development and finally it examines important new directions aimed at achieving quantum jumps in energy and power content.

© 2009 Elsevier B.V. All rights reserved.

Contents

1. Introduction	2419
2. Lithium ion batteries	2420
3. Near-term progress of the lithium ion battery technology	2422
3.1. Improvements in specific energy	2422
3.2. Improvements in power	2424
3.3. Improvements in safety and reliability	2425
4. New generation lithium ion batteries	2426
5. The lithium batteries of the future	2427
6. Conclusion	2429
Acknowledgement	2429
References	2429

1. Introduction

The present energy economy based on fossil fuels is at a serious risk due to a series of factors, including the continuous increase in the demand for oil, the depletion of non-renewable resources and the dependency on politically unstable oil producing countries. Another worrying aspect of the present fossil fuel energy economy is associated with CO₂ emissions, which have increased at a constant rate, with a dramatic jump in the last 30 years, the CO₂

level has almost doubled passing from 1970 to 2005, this resulting in a rise in global temperature with associated series of dramatic climate changes.

The urgency for energy renewal requires the use of clean energy sources at a much higher level than that presently in force. The CO₂ issue, and the consequent air pollution in large urban areas, may be only solved by replacing internal combustion engine (ICE) cars with ideally, zero emission vehicles, i.e. electric vehicles (EVs) or, at least, by controlled emission vehicles, i.e. full hybrid electric vehicles (HEVs) and/or plug-in electric vehicles (PHEVs).

Accordingly, investments for the exploitation of renewable energy resources are increasing worldwide, with particular attention to wind and solar power energy plants (REPs), which are the most mature technologies. The intermittence of these resources

* Corresponding author.

E-mail address: bruno.scrosati@uniroma1.it (B. Scrosati).

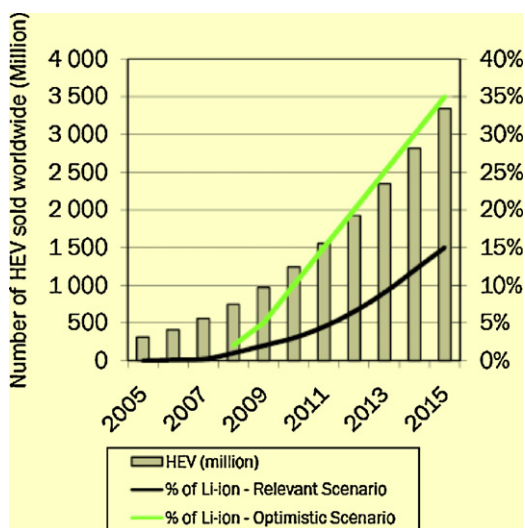


Fig. 1. HEV market evolution. By kind permission of Dr. Christophe Pillot, Avicenne Développement.

requires high efficiency energy storage systems. Electrochemical systems, such as batteries and super capacitors, that can efficiently store and deliver energy on demand in stand-alone power plants, as well as provide power quality and load levelling of the electrical grid in integrated systems, are playing a crucial role in this field. Indeed, the advantage of the use of electrochemical storage systems has been demonstrated for both wind and photovoltaic REPs [1]. The efficacy of batteries in REPs is directly related to their content in energy efficiency and lifetime. Indeed, in virtue of their high value of energy efficiency, lithium batteries are expected to provide an energy return factor higher than that assured by conventional batteries, e.g. lead-acid batteries [2].

In addition to REPs, lithium ion batteries are also seen as the power sources of choice for sustainable transport because they are considered the best options which can effectively guarantee the progressive diffusion of HEVs, PHEVs, and BEVs at high levels [3]. In HEVs the synergic combination of ICE with an electrochemical battery provides high fuel utilization with proven benefits for fuel economy and therefore, for pollution emission control, as well as favouring driving performances which are similar if not superior to those of pure gasoline cars. Indeed, the production of battery-powered HEVs has very rapidly passed from demonstration prototypes to very successful commercial products, see Fig. 1.

However, problems of various natures still prevent the large-scale diffusions of lithium ion batteries for REP and EV applications. Several countries, including Japan, United States and Europe, are allocating large investments to support R&D programs aimed to solve these problems and thus promote the development of advanced, efficient lithium batteries [4].

The purpose of this review is to report the R&D approaches which are considered to be the most promising for leading to important breakthroughs in the lithium battery technology. We will first report on the present status of this technology, discuss the evolutions which are expected to lead to near-term new batteries and conclude with the illustration of future trends.

2. Lithium ion batteries

Lithium ion batteries are light, compact and work with a voltage of the order of 4 V with a specific energy ranging between 100 Wh kg^{-1} and 150 Wh kg^{-1} . In its most conventional structure, a lithium ion battery contains a graphite anode (e.g. mesocarbon microbeads, MCMB), a cathode formed by a lithium metal oxide

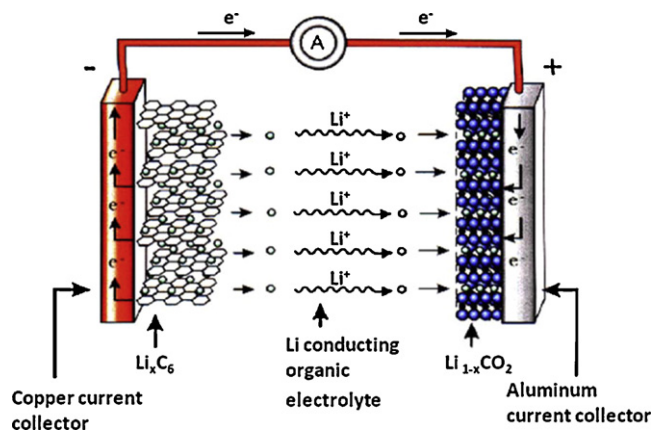
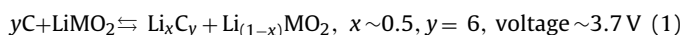


Fig. 2. Scheme of a common lithium ion battery.

(LiMO_2 , e.g. LiCoO_2) and an electrolyte consisting of a solution of a lithium salt (e.g. LiPF_6) in a mixed organic solvent (e.g. ethylene carbonate–dimethyl carbonate, EC–DMC) imbedded in a separator felt [5]. Fig. 2 shows a typical lithium ion battery configuration. In most common cases these batteries are based on the C/ LiPF_6 in EC–DMC/ LiMO_2 sequence and operate on a process:



involving the reversible extraction and insertion of lithium ions between the two electrodes with a concomitant removal and addition of electrons.

Due to the high value of the energy content, lithium ion batteries have triggered the growth of the market of popular devices, such as mobile phones, lap-top computers, MP3s and others. Indeed, lithium ion batteries are today produced by billions of units per year, see Fig. 3.

At first sight, the electrochemical process which drives the lithium ion battery appears quite simple, apparently consisting of the reversible exchange of lithium ions between the two electrodes. However, in practice the operation of this battery requires the ongoing of key side processes. In Fig. 4A we can see that the redox process at the MCMB anode evolves around 0.05 V vs. Li and that of the LiCoO_2 cathode evolves at about 4 V vs. Li. The onset of the current in the electrolyte reveals the occurrence of either reductive or oxidative decomposition processes that define its stability domain. The figure shows that the electrolyte domain extends from about 0.8 V vs. Li to 4.5 V vs. Li and that the MCMB anode operates well outside the stability of the electrolyte and the cathode is just at its limit.

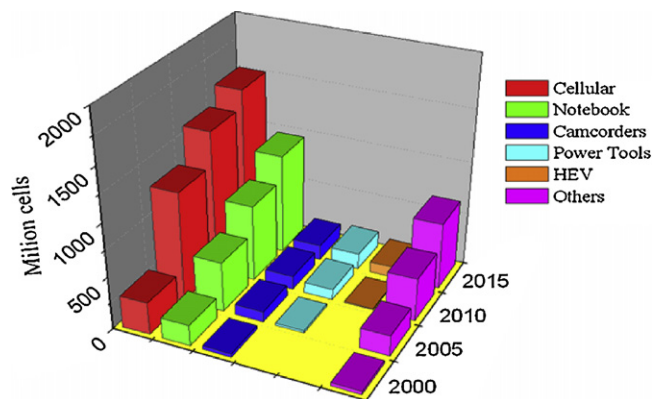


Fig. 3. Evolution of the lithium ion battery sale in the consumer electronic and HEV market.

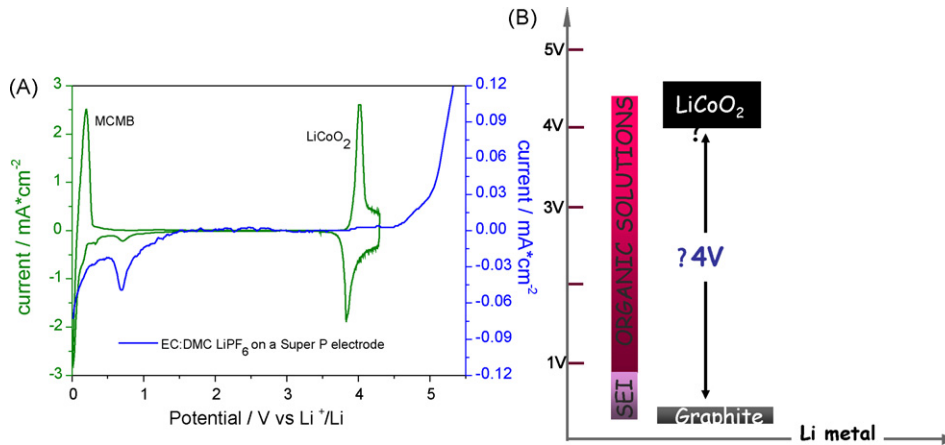


Fig. 4. (A) Cyclic voltammograms profiles (potential vs. Li/Li⁺) of lithium ion battery components: anode and cathode (green), electrolyte (blue). Counter electrodes: super P carbon; electrolyte: EC-DMC, LiPF₆. (B) Voltage operation ranges of the C/LiCoO₂ electrode combination in comparison with the stability domain of most common liquid electrolytes.

This is also clearly visible from Fig. 4B that shows the voltage ranges of the MCMB anode and the LiCoO₂ cathode in comparison with the stability window of the most common organic liquid electrolytes. We can then conclude that the C/LiCoO₂ battery is thermodynamically unstable in these electrolytes. However, in practice, the battery operates under a kinetic stability: the initial decomposition of the electrolyte results in the formation of a protective film on the anode surface, this providing the condition to assure the continuation of its charge and discharge processes. More dangerously serious are the oxidative processes at the cathode side.

Under proper conditions the battery operates below the oxidative limit of the electrolyte. However, if by unexpected events, such as accidental overcharge, this limit is exceeded, no protecting film is formed on the cathode and the electrolyte continues to oxidize, this greatly contributing to accelerate cell failure.

Overall, both the anode and the cathode decomposition processes imply consumption of active masses and of electrolytes, accompanied by gas evolution, see Fig. 5. This results in a loss of the battery capacity (initial irreversible capacity) and in safety hazards. Both capacity loss and gas evolution are of course undesired

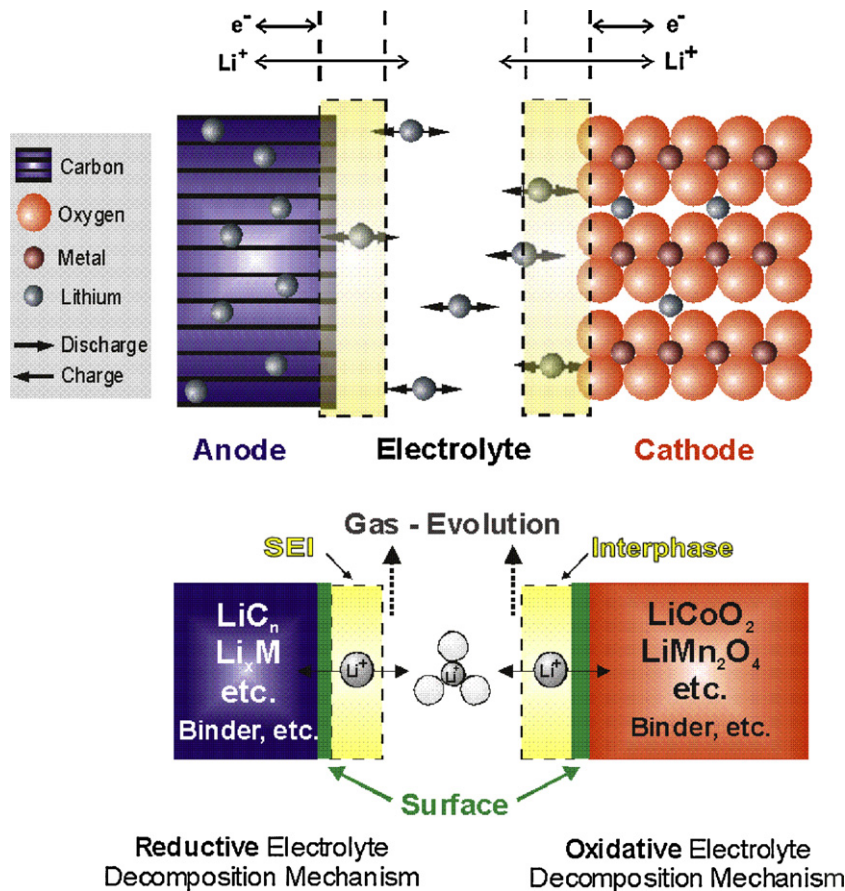


Fig. 5. Operational principle of SEI formation in a C/LiCoO₂ lithium ion battery. Taken from “Report of the Basic Energy Science Workshop on Electric Energy Storage”, Department of Energy, USA, http://www.sc.doe.gov/bes/reports/files/EES_rpt.pdf.

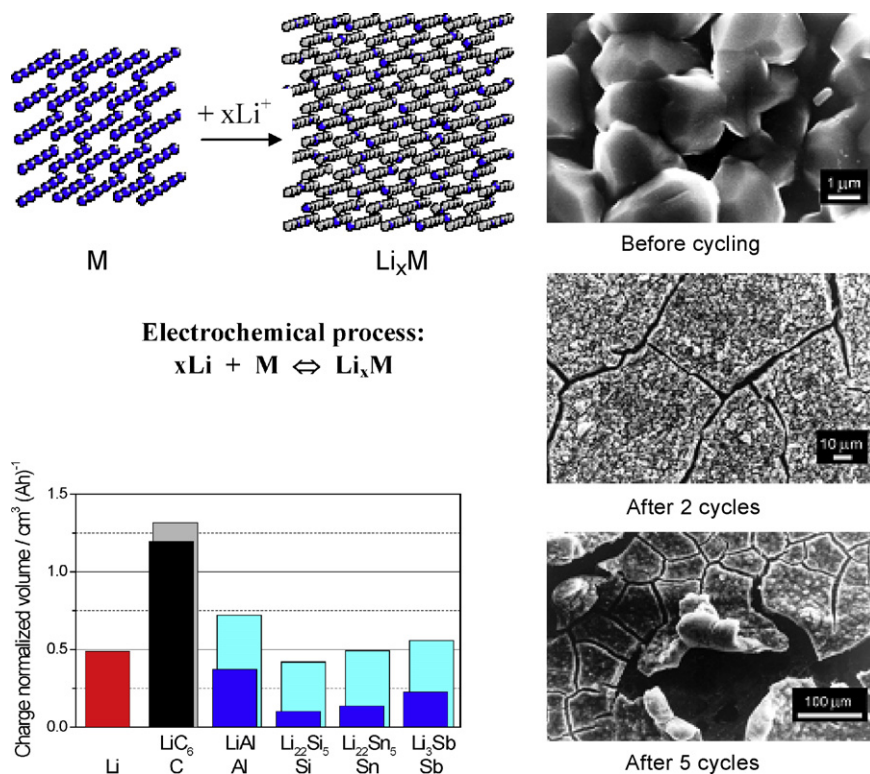


Fig. 6. Volume change effects associated to the charge and discharge process of metal alloy electrodes in lithium cells. The figure shows: scheme of Li ion insertion and related volume change during discharge (upper left); comparison of volume changes: pristine material (dark coloured columns) Li^+ intercalated material (light coloured columns) (low left) and SEM image of LiM before and after cycling (right). Taken from Ref. [7].

phenomena which must be carefully controlled (especially during the production process) to assure proper battery performance [6].

3. Near-term progress of the lithium ion battery technology

Scaling up the chemistry of common lithium ion batteries in view of their application for sustainable vehicles, or for renewable energy plants, is problematic. Barriers of various natures still prevent this important step. They include safety, cycle life, cost, wide temperature operational range and materials availability. On the other hand, the intrinsic benefit of lithium technology and its use in these key evolving markets, have triggered worldwide efforts to solve these problems in order to place the lithium ion battery in a dominant position in both EV and REP sectors.

It is now universally accepted that breakthroughs in lithium battery technology require innovative chemistries for both the electrode and the electrolyte components. The goal is to identify materials having performances higher than those offered by the anode and the cathode used in the common versions. Indeed, the chemistry of lithium ion batteries has not changed consistently since their introduction in the market in the early nineties. As already mentioned, most production still relies on a graphite anode and a lithium cobalt oxide cathode, separated by a liquid solution of a lithium salt, e.g. $LiPF_6$, in an organic solvent mixture, e.g. EC–DMC. Generally, the performance of any device directly depends on the properties of the materials on which it is formed; this is also true for lithium batteries. Thus, steps ahead for rechargeable lithium batteries can only be achieved by a breakthrough in electrode and electrolyte materials.

Accordingly, worldwide research and development efforts are directed toward the replacement of the present battery compo-

nents with materials having higher performance in terms of energy, power, cost, reliability, lifetime and safety.

The approaches to reach this goal are focused along two main directions:

- (1) the replacement of graphite and of lithium cobalt oxide with alternative, higher capacity, lower cost anode and cathode materials;
- (2) the replacement of the organic carbonate liquid electrolyte solutions with safer and more reliable electrolyte systems.

3.1. Improvements in specific energy

So far the specific energy of lithium ion batteries has been increased mainly by fabrication improvements, by using progressively lighter cases (e.g. passing from stainless steel to aluminium), or by the optimization of the cell design such as to increase the loading of active electrode materials. A limit has now been reached beyond which further increases in specific energy require modification of the cell chemistry.

Lithium metal alloys, e.g. lithium–silicon (Li–Si), and lithium–tin (Li–Sn), alloys, are among the most promising negative electrodes to replace common carbon based materials. These alloys have a specific capacity which largely exceeds that of lithium–graphite, i.e. about 4000 mAh g^{-1} for Li–Si and 990 mAh g^{-1} for Li–Sn, versus 370 mAh g for Li–C. Unfortunately, lithium alloys cannot be used as such in lithium cells, the main issue being the large volume expansion–contraction which occurs during the charge–discharge processes; these volume changes induce mechanical stresses with the resulting disintegration of the electrode with consequent failure in the round of cycles [7], see Fig. 6.

The problem has been circumvented by optimizing the electrode morphology with the development of nanostructured configura-

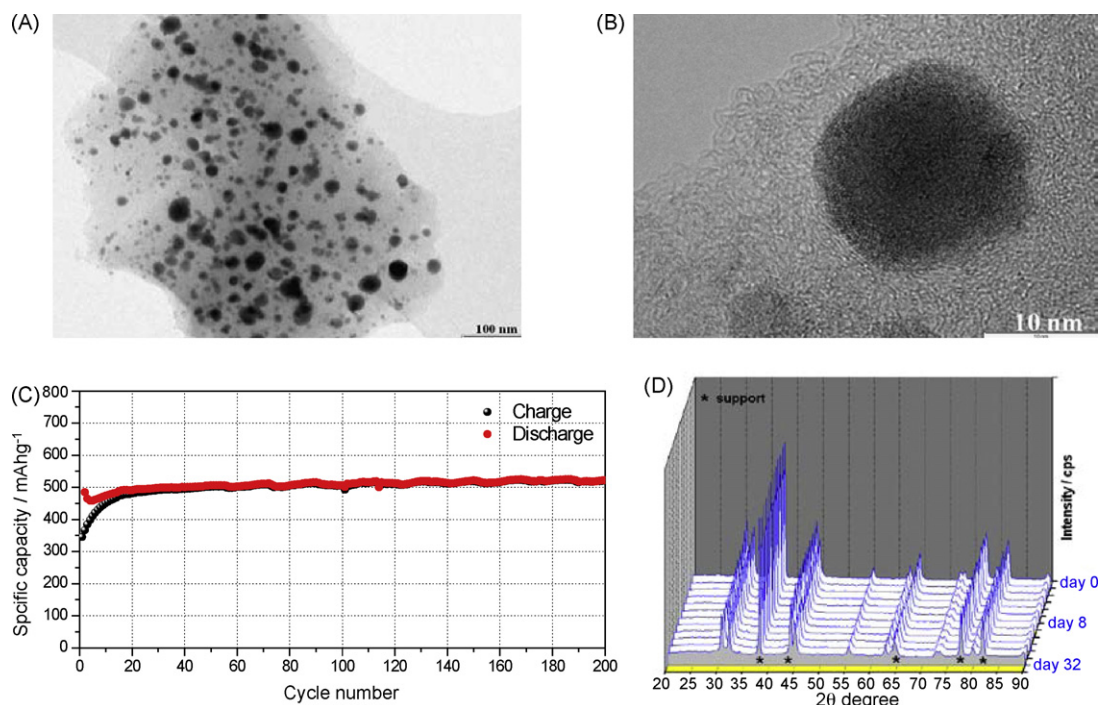


Fig. 7. Structure and performance of the Sn-C composite electrode. (A) TEM image showing the electrode morphology; (B) HRTEM image showing a Sn particle embedded in the C matrix; (C) capacity delivery versus charge–discharge cycles, and (D) evolution of XRD patterns of the Sn-C powder kept over one month under laboratory atmosphere. Taken from Refs. [8,9].

tions capable of buffering the large volume changes and thus, of assuring long cycle life combined with high specific capacity. A good example is provided by electrode structures based on metal carbon nanocomposites (e.g., tin–carbon) [8,9], see Fig. 7. In this nanostructure, the carbon matrix has a twofold, key role: (i) it provides enough free volume to accommodate expansion–contraction of the tin, assuring cycling stability and (ii) it acts as a protecting shell, assuring the safe handling of the electrode nanopowders. Fig. 7A shows the average distribution of the tin nanoparticles in the carbon matrix and Fig. 7B the appearance of a single tin particle. Fig. 7C demonstrates the high electrochemical stability of the Sn-C nanocomposite electrode that undergoes deep discharge/charge cycles with no capacity fading for over two hundred cycles. Fig. 7D reports the evolution of XRD patterns of a Sn-C nanocomposite sample maintained for more than a month in open air at room temperature: no changes in the patterns are observed, this demonstrating the high chemical stability of the nanocomposite structure.

Similar approaches have been adopted to promote the performance of Li–Si metal electrodes [10]. Results obtained by various laboratories worldwide have demonstrated that long cycle lives can be achieved by exploiting suitable electrode modifications, e.g. based on silicon–carbon composites, nanowires morphologies and 3D porous particles [11]. Because of these important achievements, the lithium metal alloys are now ready to begin lithium battery production. One example, formed by a ternary Sn–Co–C alloy, is already in use as new anode material in a commercial battery [11]. Actions for promoting enhancement at the anode side are also addressed to modification of graphite by covering the surface with thin metal layers. It is expected that this treatment, by promoting conductivity enhancement, may lead to improved electrode performance—especially in the low temperature range [12].

Research for new anode materials is also addressed to titanium oxides. In this range of materials, anatase titanium oxide TiO_2 (TO) [13] and lithium titanium oxide, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) [14] are attractive negative electrodes for advanced lithium ion batteries. The lithium insertion potential of these oxides is between 1.2 V and 2.0 V vs.

Li, i.e. within the stability window of common organic electrolytes. (Courtesy of Dr. Michel Armand, Université Jules Verne, Amiens, France). LTO has a lithium-rich, spinel-framework structure. This electrode material is characterized by a two-phase electrochemical process evolving with a flat voltage profile. The theoretical capacity is lower, and the voltage level higher, than those of conventional graphite, i.e. 170 mAh g^{-1} versus 370 mAh g^{-1} and 1.5 V vs. Li versus 0.05 V vs. Li, respectively. Both differences may result in lower specific energy; however, the interest in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ remains high because of its specific properties that include: (i) a very low volume change (<1%) during cycling, which leads to high cycling stability; (ii) no electrolyte decomposition and thus, no SEI formation, (iii) high rate and very low temperature charge/discharge capability and (iv) high thermal stability in both the charged and discharged state. Indeed, LTO is presently practically exploited to develop batteries for PHEVs [15].

Titanium oxide, TO, has a brookite structure. This anode material offers important advantages in term of cost effectiveness, safety and environmental compatibility. Its maximum theoretical capacity is 335 mAh g^{-1} , corresponding to the insertion of one Li per TiO_2 , associated with a complete $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ reduction. The electrochemical performance of TO strongly depends on the particles' morphology; consequently, the research on this material is focused on fabrication process suitable to produce it in nanosized or nanotextured forms [14,16]. Fig. 8 shows valid examples of these TO advanced nanostructures. Attempts to develop morphologies offering effective electronic conductive networks with the goal of increasing the mass utilization and electrode kinetics are also in progress [13].

Regarding cathodes, the materials of main interest for battery manufactures are today manganese-based compounds and olivine lithium metal phosphates. In the former series, a promising candidate is lithium manganese spinel, LiMn_2O_4 . In view of its favourable properties that include material availability and environmental compatibility, this manganese oxide appears as an almost ideal substitute for the common, high cost and partially toxic, lithium

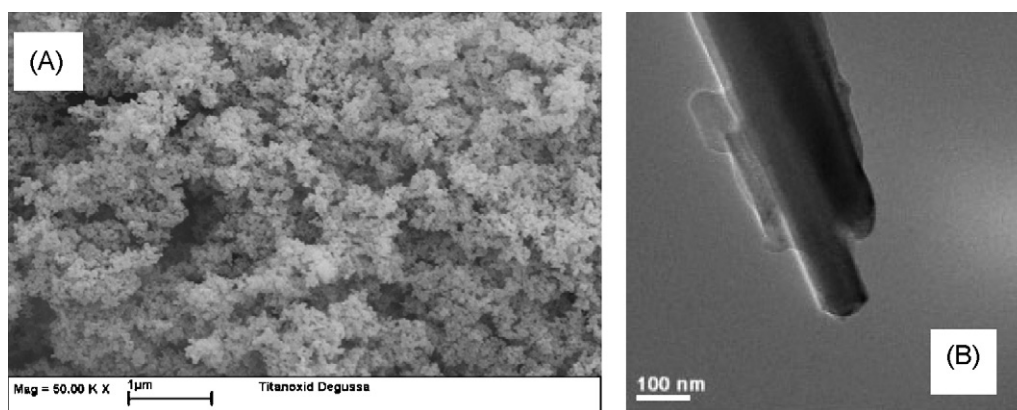


Fig. 8. TEM images of TiO_2 anatase electrodes having mesoporous (A) and nanowire (B) nanoconfigurations. Taken from Refs. [14,16].

cobalt oxide. Unfortunately the wide use of lithium manganese spinel is limited by some operational issues, the most serious being manganese dissolution into the electrolyte upon cycling in lithium cells, especially at temperatures above ambient [17,18]. This phenomenon reflects in a poor cycle life of the cell and then, the practical use of this cathode is limited to niche markets.

On the other hand, there are various strategies to be attempted for circumventing the dissolution issue. The most common include: (i) the partial substitution of manganese ions by a series of foreign ions [19–21] and (ii) surface modification by oxide coating [22,23]. Although not yet totally successful, these approaches provide concrete expectance that the route for making LiMn_2O_4 commercially viable will soon opened.

Another promising example in the manganese family is the lithium nickel manganese oxide, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which adopts a spinel structure [24]. This material is characterized by a two-phase electrochemical process reflecting in a flat voltage profile evolving around 4.5 V vs. Li. The theoretical specific capacity is 146 mAh g^{-1} , i.e. of the same order as the conventional lithium cobalt oxide, LiCoO_2 . However, the key difference is in the high operational voltage, which makes $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ a very interesting material due to its potentiality of assuring substantial increase in energy density, such as 30% more than that associated with conventional lithium manganese spinel. On the other hand, the practical use of this cathode material may be prevented by the lack of suitable electrolyte media, since the presently available organic carbonate electrolyte solution are not totally compatible with the high voltage of the lithium nickel manganese oxide, especially in the course of its charge process. R&D projects are under way to develop more stable electrolytes, so that to make this interesting cathode material viable for industrial use.

The other compound in the manganese family which has attracted considerable attention is the nickel cobalt manganese oxide, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. This material has a layered structure and operates via a typical lithium insertion–de-insertion electrochemical process, characterized by a sloping voltage averaging around 3.8 V vs. Li [25]. The practical specific that of LiCoO_2 , i.e. $160\text{--}170 \text{ mAh g}^{-1}$ vs. 140 mAh g^{-1} .

In the search of new cathodes, attention is addressed to materials of the olivine family—in particular lithium iron phosphate, LiFePO_4 (LFP) [26]. This interest is motivated by the many appealing features of this compound which include: (i) reasonably high capacity (170 mAh g^{-1}); (ii) a two-phase electrochemical process which evolves with a flat 3.5 V vs. Li voltage; (iii) a cost which in principle is lower than that of LiCoO_2 and most significantly (iv) a high intrinsic safety (the strength of the P–O covalent bond rule out any risk of oxygen release). On the other hand, LFP suffers from a very high intrinsic resistance which requires special electrode prepara-

tions, the most common involving carbon coating processes to increase the conductivity such as to assure full capacity and high rate delivery. Carbon-coated LFP is an attracting cathode material for application in batteries designed for high power applications. Effectively, LFP is already in commercial use in batteries for power tools, small vehicles and PHEVs. On the other hand, because of the low values of the tap density and of the operational voltage, LFP suffers from low volumetric energy density and thus, is not appropriate for applications that require high energy such as those directed to EVs. Attention is also focused on alternate olivines, such as LiMnPO_4 and LiCoPO_4 .

3.2. Improvements in power

Common lithium ion batteries are based on intercalation electrodes with an electrochemical process involving the removal–insertion of lithium ions between anode and cathode via transport across the electrolyte. The rate determining step of this process is the lithium diffusion in and out of the electrode structures. Thus, to improve kinetics, new, nanostructured electrode morphologies, such as nanoparticles, nanofibers and others having at least one nanometric dimension, have been considered [27,28]. It is expected that evolution to nanostructures may result in the reduction of the diffusion length of the lithium ions in and out of the electrode (see Fig. 9), and thus, in the enhancement of

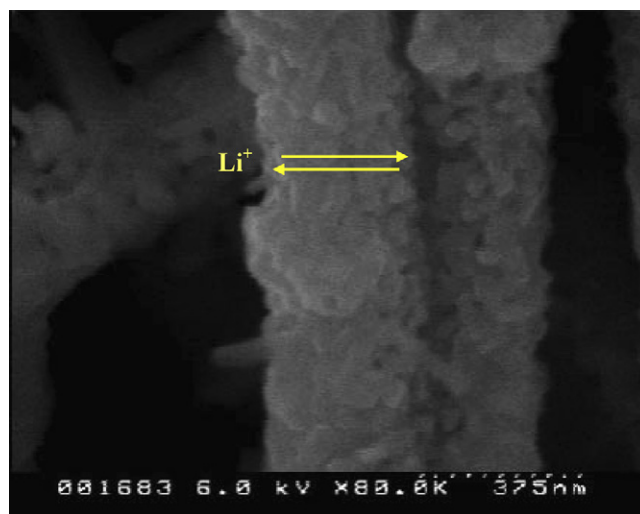


Fig. 9. Scheme of the role of nanofibers in reducing the diffusion length of the lithium ion in the electrode bulk.

the electrode charge–discharge rates. An example of this approach applies to the LFP electrode material, where the Li ions are expected to move into the bulk only along the [0 1 0] crystal direction [29]. Increases in diffusion, and thus in rate capability, can be obtained by suitable modifications, such as by inducing a coating of the LFP particle surface with a fast-ion conducting phase, formed via a controlled off-stoichiometry [30].

On the other hand, because of the large surface-to-volume ratio, the use of nanostructures is expected to result in an increase of the electrochemical active surface for the same geometrical surface by many orders of magnitude, thus making the “real” current density lower for the same total current (namely the power), that the battery can generate. In addition, the low tap density of these large surface area structures depresses the volumetric energy density and increases the reactivity of the battery to an unacceptable level. Accordingly, in same case it is more convenient to stick with conventional electrode morphologies and achieve high rate by a proper cell design, e.g. involving the reduction of the electrode thickness.

Generally, research on nanomaterials requires the design of new electrode formulations and preparation techniques. Very promising in this respect are the low temperature synthesis of tailor-made LiFePO_4 powders via the use of basic media [31], microwave procedures [32], as well as others. The identification of appropriate binders and conductive additives is also an important step in lithium battery technology. To improve electronic transport within lithium battery electrodes, carbon black is normally used as a conductive additive. This additive is not well suited for nanomaterials. The process for achieving homogenous dispersions complex and carbon black tends to disintegrate from the electrode during cycling. Thus, to ensure good cycling stability within the electrode structure, binders and additives must be properly adapted and modified.

3.3. Improvements in safety and reliability

Safety is a serious issue in lithium ion battery technology; consequently, many approaches are under study with the aim of reducing safety hazards; unfortunately, all them are expected to depress the specific energy. Thus, the practical value of these approaches depends on whether an acceptable compromise between energy and safety can be achieved. A possible strategy is that of using electrode combinations operating within the stability window of the electrolyte. A good choice is LTO, which evolves with a flat voltage plateau at 1.5 V vs. Li at the anode side and LFP which evolves around 3.5 V vs. Li, at the cathode side, see Section 4.

The electrolyte is the third component critical for the safety of lithium batteries. Concerns on the present LiPF_6 -organic carbonate solution electrolyte are: (i) the relatively narrow stability domain which prevents the use of high voltage cathodes; (ii) the high vapour pressure and the flammability which affects safety and (iii) the incompatibility with the environment and the human health, which results in serious manipulation hazards. Considerable effort is underway to improve the safety and reliability of the Li battery electrolytes, including: (i) additives to build-up stable SEI and/or enhance its thermal stability; (ii) redox shuttles to protect from overcharge, (iii) shut-down separators to prevent thermal runaway and (iv) lithium salts as an alternative to LiPF_6 , to reduce toxicity.

Other more radical approaches consider discarding the unsafe, liquid organic solutions to pass to more inert systems, ideally solvent-free lithium conducting membranes. The benefits are substantial: the passage to a solid configuration gives concrete promise of increasing cell reliability and, at the same time, of offering modularity in design and ease of handling. A sizeable bibliography exists on polymer electrolytes for lithium batteries. The interested

reader may find details in a series of excellent reviews, in which the main achievements in the field are thoroughly discussed and evaluated [33,34]. Here we will comment briefly on the most promising options. A very appealing possibility is obviously that which sees the use of a fully solid, solvent-free membrane. Although various polymer systems of this kind have been proposed, interest today concentrates on membranes based on homopolymers, such as poly(ethylene oxide), PEO, hosting a lithium salt, LiX, e.g. lithium trifluoromethanesulfonate, LiCF_3SO_3 .

By combining chemical inertness with reasonably good lithium ion transport, the PEO-LiX membranes meet in principle the main requirements as efficient electrolyte separators. In addition these membranes allow the use of metal lithium anodes, with important reflections in terms of enhancement in specific energy. Unfortunately, the ionic conductivity of the membranes remains at high levels only at temperatures above 70 °C and this is the main issue which has so far prevented their wide practical use. Many studies have been carried out with the aim of solving this issue. Some progress has been achieved by dispersing selected ceramic additives at the nanoparticle size in the polymer bulk [35], widening the useful range of temperature however, not yet to a level to make the PEO-LiX membranes suitable for batteries expected to operate at ambient and sub-ambient temperatures.

On the other hand, the high temperature of operation does not totally rule out these membranes from practical applications in lithium batteries, especially if these are directed to the automobile sector where temperature may not be a critical factor. Accordingly, relevant projects have been launched in the 90s for the development of lithium polymer batteries. The interest in this technology has partly vanished since then. However, the concept of a fully solid, lithium metal polymer battery is still very appealing and is presently being considered in industrial laboratories involved in electric transportation [36].

Normally there is some concern on the use of the energetically attractive metallic Li electrode because of the risk of dendrite formation [37] caused by not uniform Li-plating, e.g. deposition on nanoscale protrusions. This could be partially prevented if a solid polymer electrolyte with ceramic stiffening additives [35], such as silica powder [38], is used adjacent to the metal. Present focus is on composite electrolytes combining stiffness with high ionic conductivity, as for example block copolymers or conducting glasses.

The intrinsic value of the polymer electrolyte concept continues to hold industrial interest and some compromise approaches have been adopted while in expectation of a breakthrough in solvent-free membranes. The most common compromise involves the use of solid-liquid hybrids formed by trapping typical liquid lithium ion solutions (e.g. LiPF_6 -carbonate solvent mixtures), in a polymer matrix, e.g. poly(acrylo nitrile), PAN or poly(vinylidene fluoride), PVDF, to form gel-type polymer electrolytes, PGEs. The PVDF-HFP-based membrane, developed at Bellcore, paved the way for the evolution of these polymer membranes [39].

Also for this class of materials there is sizable literature where the properties and characteristics PGEs are thoroughly described [40,41]. The main feature is the high conductivity, nearly matching that of a pristine liquid solution; on the other hand, issues typically associated with the presence of the liquid, e.g. safety and reliability, cannot be completely avoided. Nevertheless, GPEs are presently used by various battery manufactures for the fabrication of the so called “lithium ion polymer batteries”, LiPBs. Relevant examples are those currently under production in Japan, either using a flame-retardant GPE with a low content of PVDF-HFP polymer matrix [42] or a GPE based on a mixture of cross-linkable polyalkylene oxide polymers [43].

Another, emerging class of electrolytes is that based on ionic liquids, namely, low temperature molten salts having important

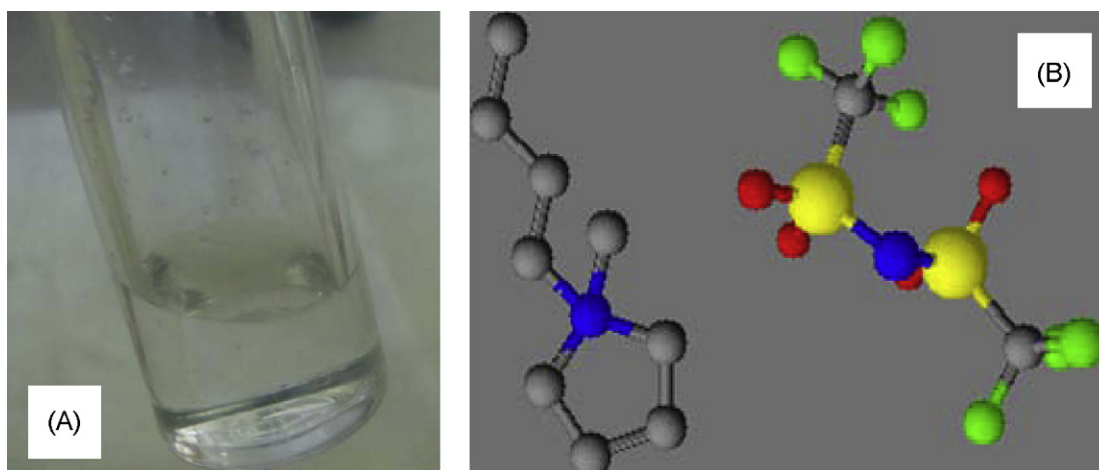


Fig. 10. Typical appearance of an ionic liquid (A) and formula structure of a typical example formed by a 1-butyl-1-methylpyrrolidinium cation in combination with bis(trifluoromethanesulfonyl)imide anion (B).

specific properties (Fig. 10). Typically, ILs are formed by the combination of a weakly interacting, large cation, e.g. of the imidazole type and a flexible anion, e.g. N,N-bis(trifluoromethanesulfonyl)imide (TFSI) [44]. ILs are non-volatile, non-flammable, highly conductive, environmentally compatible and can safely operate in a wide temperature range. This unique combination of favourable properties make ILs very appealing materials as stable and safe electrolyte media in lithium batteries [44]. Many laboratories worldwide are engaged in the investigation of ILs with the aim of establishing their effective potential as lithium battery electrolytes [45–49]. The results, however, are in part contradictory especially in defining the electrochemical stability of lithium conducting, IL-based solutions. Most commonly it is believed that these solutions have a poor cathodic stability limit associated with the tendency of imidazolium-based cations to be reduced by electrochemical deprotonation around 1.5 V vs. Li. This apparently prevents the use of IL-based solutions with common low voltage anode materials, such as lithium metal, graphite or even $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Many studies are underway to circumvent this issue by developing ILs based on cations more resistant to reduction than those of the imidazolium family. Promising results have been obtained by shifting to aliphatic quaternary ammonium cations having no acidic protons and thus, expected to have a stability domain extending to low voltages. A good example is the IL formed by combining N-n-butyl-N-ethyl-pyrrolidinium cation with N,N-bis(trifluoromethanesulfonyl)imide anion having lithium N,N-bis(trifluoromethanesulfonyl)imide as the dissolved lithium salt [50]. Another emerging class of ILs for batteries is using FSI instead of TFSI as anion.

One drawback of ionic liquids is in their cost still prohibitively high, although price reduction is expected if the production will be scaled up. In the meantime, given to the actual high cost, it is likely that ILs, rather than full electrolyte media, will be used as additives to the common organic liquid electrolyte solutions [51,52].

4. New generation lithium ion batteries

Most of the materials described in the previous section are on their way to be used as alternate electrodes or electrolytes in new lithium ion battery configurations. In most cases, however, the innovation only concerns a single component, either the anode, the cathode or the electrolyte, while the others remain unchanged, reproducing the conventional structure. A current approach, adopted in many emerging commercial batteries, considers innovations which involve the cathode only. Most popular is

that seeing the replacement of lithium cobalt oxide by lithium iron phosphate, still maintaining conventional chemistry at the anode and at the electrolyte. Since LFP is safer and cheaper than LiCoO_2 its use as cathode may improve the battery reliability and partially decrease its cost; however, preservation of the graphite and, particularly, of the unstable liquid organic electrolyte does not exclude safety risks for the overall battery.

The C/ LiFePO_4 batteries are on the selling list of many battery manufacturers in Europe, Asia and United States aiming to meet the requirement of some niche electronic market and, in most of the cases, to enter in the race for supplying the HEV. Indeed, various joint ventures between lithium battery manufacturers and car companies are underway to marketing lithium battery-powered, HEVs and PHEVs. Although the chemistry of the lithium batteries to be used in these projects is generally not released, it is reasonable to suppose that in most cases is lithium iron phosphate the cathode of choice.

More enterprising manufacturers are considering to develop batteries with two innovative components, usually the anode and the cathode. Batteries using electrode combinations which are expected to operate more safely than the present C- LiCoO_2 are valid examples of this second, new class of advanced lithium ion batteries. Most commonly these batteries exploit a LTO-LFP couple maintaining the standard LiPF_6 -carbonate solvent, liquid electrolyte. As already mentioned, both electrodes operate within the stability domain of the electrolyte, see also Fig. 11 and thus,

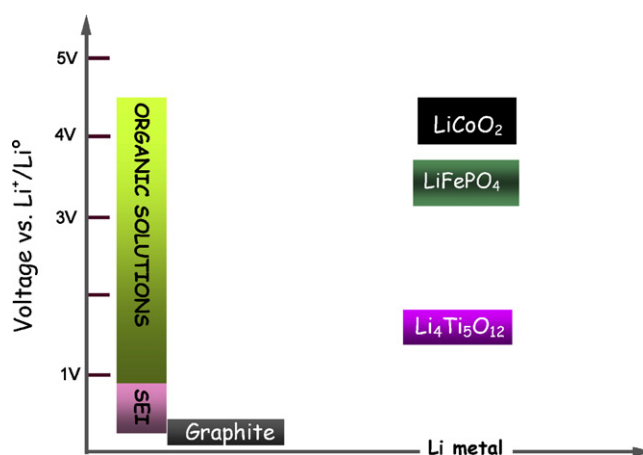


Fig. 11. Voltage vs. Li^+/Li^0 of various electrode materials in comparison with the stability window of common liquid organic electrolytes.

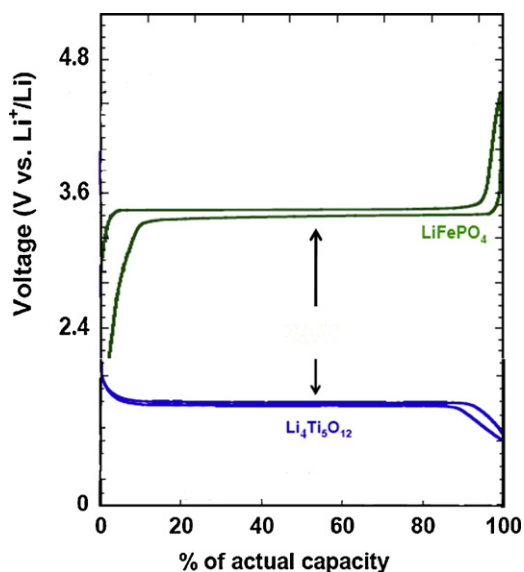


Fig. 12. Voltage charge–discharge profiles for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – LiFePO_4 lithium ion battery.

expected to gain reliability in respect to the conventional C– LiCoO_2 chemistry.

By combining the 1.5 V $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode with the 3.5 V LiFePO_4 cathode, lithium ion batteries, operating in the 2 V range may be obtained (see Fig. 12). These batteries, whose concept was originally conceived and experimentally proved in academic laboratories [53–55] are now under consideration for market production by battery manufacturers.

A possible criticism of these batteries is in their voltage level, which is lower than that of the conventional C– LiCoO_2 system. However, this apparent shortcoming is counterbalanced by enhanced safety and, possibly, by cost reduction, i.e. by the two aspects which are among the most crucial for assuring the use of lithium ion batteries in emerging markets. In addition, it must be noted that the voltage may be raised to higher levels by properly redesigning the electrode combination, that is by replacing the 3.5 V LiFePO_4 with a higher voltage cathode; the choice is wide and there are various possible candidates for this upgrading strategy, see Fig. 13. The 2.5 V $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$, Li ion technology [56] and the 3.0 V $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cell [57], are two possible candidates for such an upgrade.

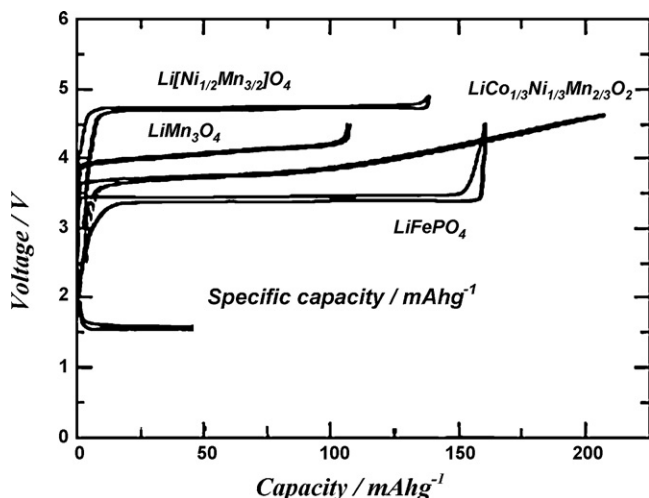


Fig. 13. Voltage charge–discharge profiles of a lithium titanium oxide anode and of various cathode materials.

The renewal of the electrode component is certainly a step ahead for the progress of lithium ion battery technology. However, even with the replacement of both anode and cathode, complete trust in battery performance cannot be assured since some of the issues associated with the conventional chemistry may not be totally preventable. The liquid organic solution, still used as the electrolyte in the separator, may be a source of unpredictable reactions which may also affect the safety of the battery.

The real breakthrough in the field is in revolutionary battery designs in which all the three conventional components are removed in favour of alternative, more efficient and safer materials. To our knowledge, no one of these totally renewed batteries has yet found its way to commercial development, with the possible exception of the SONY Nexelion battery [11], although it is not clear whether the cathode adopted by SONY is actually a new concept.

Yet, this mission is not impossible: the large variety of materials available from the vast literature of lithium ion batteries offers real possibilities for identifying the right formulation for advanced battery types. The obvious approach is to exploit configurations which use renewed electrode combinations (as those above discussed), combined with the replacement of conventional liquid electrolyte solutions with a more stable polymer electrolyte. Examples that confirm the validity of this approach are available; a good one is the lithium ion polymer battery using a TiO_2 anode and a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode separated by a PVDF-based gel electrolyte [58]. By combining the advantages of the electrode combination (safe operation, long life) with those of the electrolyte (plasticity, high conductivity), this battery is expected to provide excellent performance, as indeed experimentally demonstrated, see Fig. 14.

Another relevant example is given by the battery exploiting the $\text{SnC}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode combination in conjunction with a GPE [59]. Fig. 15 provides evidence for the excellent performance of the battery in terms of rate capability and cycle life.

The examples here reported demonstrate that by a clever choice of the new electrode and electrolyte materials presently available, new types of advanced lithium ion batteries may effectively be developed.

5. The lithium batteries of the future

Lithium batteries are one of the great successes of modern electrochemistry. These batteries have an established role in the consumer electronic market with no risk of replacement by any other contender and, by intelligent modification of the electrode and electrolyte components, they will soon also dominate the electric automotive transportation and renewable energy storage markets. The potential of these unique power sources make it possible to foresee an even greater expansion of their area of applications to technologies that span from medicine to robotics and space, making lithium batteries the power sources of the future.

To further advance in the science and technology of lithium batteries, new avenues must be opened. Changes in the chemical structures, as described herein, are not sufficient. Further improvements in safety, environmental sustainability and energy content are mandatory; these can only be obtained by totally renewing the lithium battery concept, so far mostly based on insertion chemistry. Although the insertion electrodes are based on sustainable 3d metals, such as Ti (TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$) or Fe (LiFePO_4), they are produced from ores, and thus their extraction and manipulation require constantly increasing amounts of energy. This energy consuming fabrication process poses some questions about the long term viability of lithium batteries.

In addition, insertion reactions are confined to a maximum of one electron transfer per transition metal, this greatly limit-

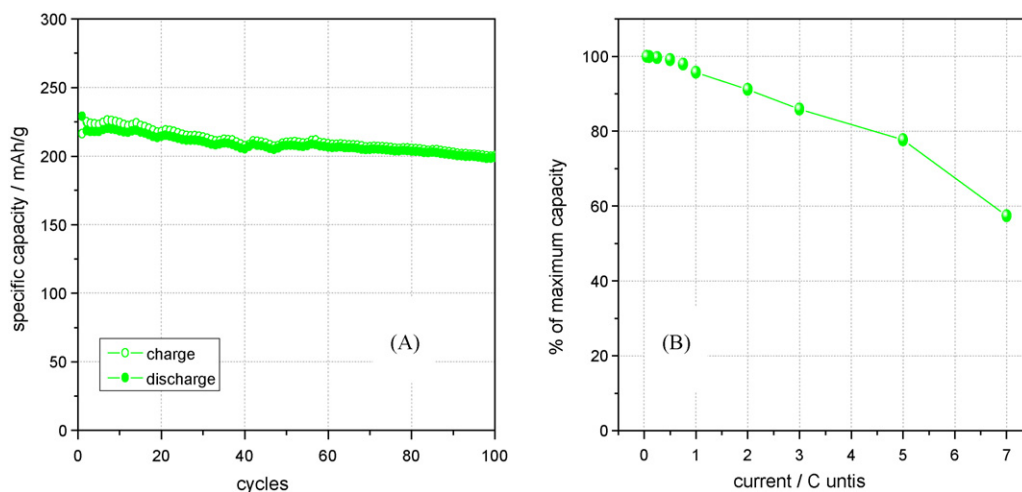


Fig. 14. Operational characteristics of a $\text{TiO}_2/\text{PGE}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery in terms of cycle life (A) and of capacity versus current rate (B). Taken from Ref. [57] by permission of the Electrochemical Soc. Inc.

ing the specific energy of the batteries. Significant increases in performance require radical changes in the fundamental electrochemical process, such as a passage from insertion to conversion chemistry which may basically assure operation implying from two to six electron transfer [60]. Simply put, the need is to pass from the classic $x\text{Li} + \text{MX}_y \rightleftharpoons \text{Li}_x\text{MX}_y$ insertion processes to new $x\text{Li} + \text{MX}_y \rightleftharpoons \text{Li}_x\text{X}_y + \text{M}$ conversion processes, although life time problems, caused by conversion related phase changes of the redox materials, cannot be overlooked.

Pioneering work of Tarascon and co-workers, introduced a search for high capacity, conversion electrode materials [61]. A reaction pathway enlisting the complete electrochemical reduction of metal oxides, sulfides, nitrides, phosphides and fluorides into a composite consisting of nanometric particles dispersed in an amorphous Li_mX ($\text{X} = \text{O}, \text{S}, \text{N}, \text{P}$), was demonstrated. However, these conversion electrodes suffered from a marked hysteresis in voltage between charge and discharge, leading to poor energy and voltage efficiency. Following this work, substantial improvement was obtained by using a metal hydride, e.g. MgH_2 , as a selected conversion electrode [62]. This electrode shows a reversible process $2\text{Li} + \text{MgH}_2 \rightleftharpoons \text{Mg} + 2\text{LiH}$, delivering a practical capacity as high 1480 mAh g^{-1} at an average voltage of 0.5 V vs. Li, combined with a very low charge–discharge polarization, both properties making it suitable for anode application in practical batteries.

The pursuit of high capacity has been addressed to other cathodes, such as the air cathode. Metal–air technologies have been exploited for a series of batteries, the most common example being the zinc–air battery. By reacting lithium directly with oxygen from

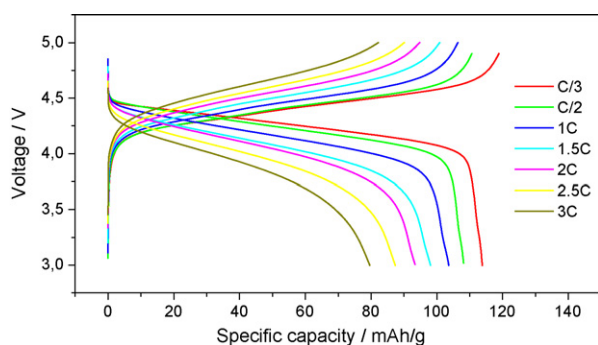


Fig. 15. Operational characteristics of a $\text{SnC}/\text{PGE}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery in terms of charge–discharge cycles at various rates (A) and of specific capacity versus cycle number at 1C (B). Taken from Ref. [59].

air, according to the reaction $2\text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$, i.e. a very high capacity of 1200 mAh g^{-1} may be obtained, a much greater value than that possibly achievable by any insertion cathode. Efficient lithium–air battery performance in terms of rechargeability has recently been demonstrated by developing a configuration that exploits a low cost, $\alpha\text{-MnO}_2$ nanowires catalyst, making possible the design of porous, three-dimensional electrodes which assure improved kinetics and energy efficiency [63], see Fig. 16. The practical development of the Li–air battery, however, is still prevented by the difficulties in mastering lithium metal and oxygen electrodes in an efficient, rechargeable and safe battery configuration. The Li anode suffers from water contamination; water, even in traces, induces serious safety risks. The air cathode is affected by problems associated with the reaction mechanism, a serious one being clogging of reaction sites by Li_2O_2 . The use of selective, high cost catalyst is then required. Vitreoceramic coating protection of the lithium anode [64] and the use of hydrophobic ionic liquid-based electrolytes [65], have been proposed to control the issues caused by occasional entry of water.

Considerable work is still needed to make the Li–air battery an immediate technological solution for high-capacity lithium batteries. Engineering and chemical advances are required to optimize the porosity, structure and composition at the cathode side and to prevent uneven lithium deposit which may lead to inherent unsafe

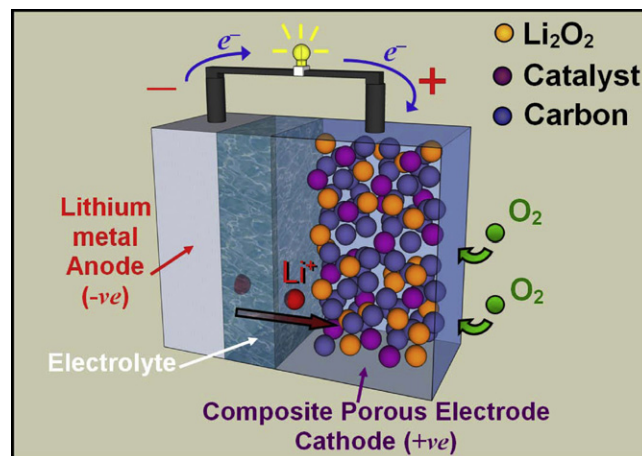


Fig. 16. Scheme of a rechargeable Li–O₂ battery. Lithium metal anode; porous $\alpha\text{-MnO}_2$ -catalyzed Li_2O_2 cathode, LiPF_6 -propylene carbonate organic electrolyte. Taken from Ref. [63].

cell operation at the anode side. Care must also be given to prevent the ingress of either CO₂ or H₂O, which can react with both the Li anode and the Li₂O₂ cathode. However, the outstanding intrinsic value of the capacity of the Li–O₂ system reinforces the importance of this battery and justifies further efforts to make it technologically viable.

Another promising candidate for high energy systems is the lithium/sulfur, Li/S battery based on the electrochemical reaction: $16 \text{Li} + \text{S}_8 \rightleftharpoons 8\text{Li}_2\text{S}$ which, assuming complete conversion, has an energy density of 2500 Wh kg⁻¹ and 2800 Wh l⁻¹ in terms of weight and volume, respectively. Although investigated by many workers for several decades [66–69] the practical development of the lithium/sulfur battery has been so far hindered by a series of shortcomings. A major issue is the high solubility in the liquid organic electrolyte of the polysulfides Li₂S_x (1 ≤ x ≤ 8) that forms as intermediates during both charge and discharge processes. The high solubility results in a loss of active mass that reflects in a low utilization of the sulfur cathode and in severe capacity decay upon cycling. The dissolved polysulfide anions, by migration through the electrolyte, may reach the lithium metal anode where they react forming insoluble products on its surface, this also contributing to depress the battery operation [70]. Various strategies to address the solubility issue have been explored. They include among others: (i) the design of modified organic liquid electrolytes [71], (ii) the use of ionic liquid-based electrolytes [72] and (iii) the use of polymer electrolytes [73]. Important progress has been recently obtained by Nazar and co-workers who showed that by fabricating cathodes based on an intimate mixture of nanostructured sulfur and mesoporous carbon, high reversible capacity and good rate can be obtained [74]. However, although promising, all these results are still far from making real breakthroughs in the Li/S battery system.

Finally, a fascinating new path in the evolution of the lithium battery is the use of organic materials by a choice inspired by common events in nature. The chemistry of life, which is mainly based on organic materials, uses renewable processes associated to the cycling of biochemical reactions, the most significant example being photosynthesis, using chlorophyll as the organic mediator. Similar to this process, the challenge is to exploit organic lithium battery electrode materials that can be synthesized by green chemistry from biomass, which is easily recyclable [60]. The basic goal is to develop lithium ion batteries by using a cycle process with no CO₂ production. A valid practical example is dilithium rhodizonate, Li₂C₆O₆ in which the redox centres at carbonyl groups can electrochemically react with four lithium ions per formula unit [75]. According to this process, Li₂C₆O₆, proceeding in tandem with lithium, delivers a specific capacity of 580 mAh g⁻¹.

6. Conclusion

Lithium battery technology evolves at a pace so rapid that evaluation of its progress may easily become obsolete. With this in mind, we have tried to give some consideration to the type of electrode and electrolyte materials that, based on their related electrochemistry, morphology and engineering design, are expected to influence the progress of these important power sources in terms of energy and cycling performance.

The relevance of the choice of materials is obvious. Crucial battery parameters, such as specific energy and power, safety and cycle life, clearly depend on the electrode and electrolyte performance. However, these can be properly enhanced, if not modified, by an optimization of their morphology. Issues such as slow electrode kinetics and damaging strains associated with large volume expansion–contraction upon cycling, can be circumvented by switching to nanostructures. In addition, nanostructures can

change the reaction pathway positively affecting capacity, power and reversibility.

We first discussed and evaluated the modifications which are expected to find their way to an industrial scale in the near future. This evolution is powered by the aggressive race among various academic and industrial laboratories to upgrade lithium batteries – mostly of the Li ion type – for the automotive industry, e.g. for HEVs, PHEVs and in prospect, EVs, as well for photovoltaic-battery power plants. Here the progress is notable to the point that new, car-compatible lithium ion batteries will soon be available. Road production of PHEVs, powered by lithium ion batteries, has already been announced by leading car manufacturers worldwide [4]. The evolution of these batteries has been pushed to meet the demands of the automotive industry; however, so far only modest changes, involving one or maximum two battery components, have been commercially proposed, always maintaining an overall chemistry based on insertion processes.

These progresses are by no means exhaustive. The evolution of the lithium ion battery is open to innovations that will place it in top position as the battery of the future. Radical changes in lithium battery structure are required. Changes in the chemistry, like those so far exploited for the development of batteries for road transportation, are insufficient. Improvements in environmental sustainability and energy content are mandatory and these can only be obtained by renewing the lithium battery concept, e.g. by passing from an insertion process to a conversion process. Freed from the constraints of insertion electrodes, in which the electrochemical process is limited to one electron per formula unit, conversion processes, which allow from two to six electron transfers per formula unit, make possible to reach high capacity, i.e. even above 1000 mAh g⁻¹. Important examples of this evolution are already in progress with the use of lithium-air and lithium-sulfur batteries [76]. However, key issues are still to be resolved and it must be kept in mind that the solution for the remaining challenges will require joint efforts from a range of interdisciplinary studies and their success will crucially depend on the efficiency of exchange of ideas and results.

Acknowledgement

One of us (J.G.) is grateful to the University of Rome Sapienza for a Visiting Professor Fellowship.

References

- [1] M. Perrin, Y.M. Saint-Drenan, F. Mattera, P. Malbranche, J. Power Sources 144 (2005) 402.
- [2] C.J. Rydh, B.A. Sandén, Energ. Convers. Manage. 46 (2005) 1957, 1980.
- [3] E. Karden, S. Ploumen, B. Fricke, T. Miller, K. Snyder, J. Power Sources 168 (2007) 2.
- [4] J. Tellefson, Nature 456 (2008) 436.
- [5] W. van Schalkwijk, B. Scrosati (Eds.), Advances in Lithium-ion Batteries, Kluwer Academic/Plenum, Boston, 2004.
- [6] Report of the Basic Energy Sciences Workshop on Electrical Energy Storage, DOE, July 2007.
- [7] M. Winter, J.O. Besenhard, Electrochim. Acta 45 (1999) 31.
- [8] G. Derrien, J. Hassoun, S. Panero, B. Scrosati, Adv. Mater. 19 (2007) 2336.
- [9] G. Derrien, J. Hassoun, S. Panero, B. Scrosati, Adv. Mater. 20 (2008) 3169.
- [10] H. Kim, B. Han, J. Choo, J. Cho, Angew. Chem. Int. Ed. 47 (2008) 1.
- [11] H. Inoue, International Meeting on Lithium Batteries IMLB 2006, June 18–23, 2006, Biarritz, France, 2006, Abstr.# 228.
- [12] M. Mancini, F. Nobili, S. Dsoke, F. D'Amico, R. Tossici, F. Croce, R. Marassi, J. Power Sources (2008), doi:10.1016/j.jpowsour.2008.10.084.
- [13] A. Ohzuko, N. Ueda, N. Yamamoto, J. Electrochem. Soc. 142 (1995) 1431.
- [14] P. Kubiak, J. Geserick, N. Hüsing, M. Wohlfahrt-Mehrens, J. Power Sources 175 (2008) 510.
- [15] www.altairnano.com; www.enerl.com.
- [16] A.R. Armstrong, G. Armstrong, J. Canalis, R. Garcia, P.G. Bruce, Adv. Mater. 17 (2005) 862.
- [17] R.J. Gummow, A. De Kock, H.M. Thackeray, Solid State Ionics 69 (1994) 59; J. Hassoun, P. Reale, B. Scrosati, J. Mater. Chem. 17 (2007) 3668.
- [18] Y. Xia, Y. Zhou, M. Yoshio, J. Electrochem. Soc. 144 (1997) 1431.

- [19] M. Hosoya, H. Ikuta, T. Uchida, M. Wakihara, *J. Electrochem. Soc.* 144 (1997) L52.
- [20] A. Amatucci, A. Du Pasquier, A. Blyr, T. Zheng, J.M. Tarascon, *Electrochim. Acta* 45 (1999) 255.
- [21] K.-S. Lee, H.J. Bang, S.-T. Myung, Y.-K. Sun, *J. Power Sources* 174 (2007) 726.
- [22] Y.-K. Sun, S.-T. Myung, K. Amine, *J. Am. Chem. Soc.* 127 (2005) 13411.
- [23] Y.-K. Sun, S.-T. Myung, B.-C. Park, J. Prakash, I. Belharouak, K. Amine, *Nat. Mater.* 8 (2009) 320.
- [24] J. Hassoun, P. Reale, B. Scrosati, *J. Mater. Chem.* 178 (2007) 3668.
- [25] P. Reale, D. Privitera, S. Panero, B. Scrosati, *Solid State Ionics* 178 (2007) 1390.
- [26] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1609.
- [27] A.S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, W. van Schalkwijk, *Nat. Mater.* 4 (2005) 366.
- [28] P. Bruce, B. Scrosati, J.-M. Tarascon, *Angew. Chem. Int. Ed.* 47 (2008) 2830.
- [29] M.S. Islam, D.J. Driscoll, C.A.J. Fisher, P.R. Slater, *Chem. Mater.* 17 (2005) 5085.
- [30] B. Kang, G. Ceder, *Nature* 458 (2009) 190.
- [31] N. Recham, M. Armand, L. Laffont, J.-M. Tarascon, *J. Power Sources* 180 (2008) 875.
- [32] S. Beninati, L. Damen, M. Mastragostino, *J. Power Sources* 180 (2008) 875.
- [33] F.M. Gray, *Solid Polymer Electrolytes*, VCH, Weinheim, 1991.
- [34] F. Gray, M. Armand, in: T. Osaka, M. Datta (Eds.), *Energy Storage Systems for Electronics*, Gordon and Breach Science Pu, 2000, p. 351.
- [35] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, *Nature* 394 (1998) 456.
- [36] www.google.com, Pininfarina-Bolloré joint venture, B0 city car.
- [37] M. Dollé, L. Sannier, B. Beaudoin, M. Trentin, J.-M. Tarascon, *Electrochem. Solid-State Lett.* 5 (2002) A286.
- [38] S. Khan, P.S. Fedkiw, G.L. Baker, DOE BATT Program Annual Review Meeting (May, 2004).
- [39] J.-M. Tarascon, S.A.S. Gozdz, C. Schmutz, F. Shokoohi, P.C. Warren, *Solid State Ionics* 86–88 (1996) 49.
- [40] J.H. Meyer, *Adv. Mater.* 10 (1998) 439.
- [41] J.Y. Song, Y.Y. Wang, C.C. Wan, *J. Power Sources* 77 (183) (1999) 183.
- [42] T. Yamamoto, T. Hara, K. Segawa, K. Honda, H. Akashi, *J. Power Sources* 174 (2007) 1036.
- [43] T. Endo, *Batteries 2008*, Nice, France, 8–10 October 2008.
- [44] A. Fericola, B. Scrosati, H. Ohno, *Ionics* 12 (2006) 95.
- [45] H. Matsumoto, H. Sakaebe, K. Tatsumi, *J. Power Sources* 160 (2006) 1308.
- [46] S. Seki, et al., *J. Phys. Chem. B* 110 (2006) 10228.
- [47] J.-H. Shin, W.A. Henderson, S. Passerini, *J. Electrochem. Soc.* 152 (2005) A978.
- [48] B. Garcia, S.G. Levallée Perron, C. Michot, M. Armand, *Electrochim. Acta* 49 (2004) 4583.
- [49] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* 8 (2009) 621.
- [50] A. Fericola, F. Croce, B. Scrosati, T. Watanabe, H. Ohno, *J. Power Sources* 174 (2007) 342.
- [51] Isikawa, et al., *J. Power Sources* 162 (2006) 658.
- [52] Saint, et al., *J. Electrochem. Soc.* 155 (2006) A172.
- [53] S. Panero, D. Satolli, M. Salomon, B. Scrosati, *Electrochem. Commun.* 2 (2000) 810.
- [54] T. Ohzuku, K. Ariyoshi, S. Yamamoto, Y. Makimura, *Chem. Lett.* 12 (2001) 1270.
- [55] P. Reale, S. Panero, B. Scrosati, J. Garche, M. Wohlfart-Meherens, M. Wachtler, *J. Electrochem. Soc.* 151 (2004) 12.
- [56] I. Belharouak, Y.-K. Sun, W. Lu, K. Amine, *J. Electrochem. Soc.* 154 (2007) A1083.
- [57] S. P-Reale, B. Panero, Scrosati, *J. Electrochem. Soc.* 152 (2005) A1949.
- [58] G. Armstrong, A.R. Armstrong, P.G. Bruce, P. Reale, B. Scrosati, *Adv. Mater.* 18 (2006) 2597.
- [59] J. Hassoun, S. Panero, P. Reale, B. Scrosati, *Adv. Mater.* (2009), doi:10.1002/adma.200900470.
- [60] M. Armand, J.M. Tarascon, *Nature* 451 (2008) 652.
- [61] P. Poizot, S. Laurelle, S. Greugon, L. Dupont, J.-M. Tarascon, *Nature* 407 (2000) 496.
- [62] Y. Oumellal, A. Rougier, G.A. Nazri, J.-M. Tarascon, L. Aymard, *Nat. Mater.* 7 (2008) 916.
- [63] A. Débart, A.J. Peterson, J. Bao, P.G. Bruce (Eds.), *Angew. Chem. Int.* 47 (2001) 4521.
- [64] S.J. Visco, E. Nimon "Lithium metal aqueous batteries" 12th International Meeting on Lithium Batteries", Nara, Japan, June 27–July 2, 2004, abstract 53; US Patent 20,041,967,641 A1 (2004).
- [65] T. Kuboki, T. Okuyami, T. Ohsaki, N. Takami, 12th International Meeting on Lithium Batteries, Nara, Japan, June 27–July 2, 2004, abstract 398.
- [66] R.D. Rauh, K.M. Abraham, G.F. Pearson, J.K. Suprenant, S.B. Brummer, *J. Electrochem. Soc.* 126 (1979) 523.
- [67] E. Peled, H. Yamin, *J. Power Sources* 9 (1983) 281.
- [68] D. Peramunage, S.A. Licht, *Science* 261 (1993) 1029.
- [69] J. Shim, K.A. Stribel, E.J. Cairns, *J. Electrochem. Soc.* 149 (2002) A1321.
- [70] S.-E. Cheon, et al., *J. Electrochem. Soc.* 150 (2003) A800.
- [71] J.H. Shin, E.J. Cairns, *J. Electrochem. Soc.* 155 (2008) A368.
- [72] L.X. Yuan, et al., *Electrochem. Commun.* 8 (2006) 610.
- [73] S.J. Jeong, et al., *J. Power Sources* 174 (2007) 745.
- [74] X. Ji, K.T. Lee, L.F. Nazar, *Nat. Mater.* 8 (2009) 500.
- [75] M. Armand, S. Grugeon, H. Vezin, S. Laurelle, P. Ribiere, P. Poizot, J.-M. Tarascon, *Nat. Mater.* 8 (2009) 120.
- [76] J. Hassoun, B. Scrosati, Italian Patent pending.