Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries†

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In the race for better Li-ion batteries, research on anode materials is very intensive as there is a strong desire to find alternatives to carbonaceous negative electrodes. A large part of these studies is devoted to alloying reactions, which have been known for more than thirty years but that have regained great interest by downsizing particle sizes, moving to nano-textured/nanostructured composites, or designing new electrode concepts. It is not the scope of this review to retrace twenty-five years of research, but rather to highlight recent advances that have been made in the use of Sn or Si-based electrodes together with the remaining challenges to be addressed and issues to be solved prior to such electrodes being commercially implemented in Li-ion cells.

Introduction

As shown in the bar chart presented in Fig. 1, the field of anode materials for Li-ion batteries is the subject of a constantly increasing number of publications, patent applications and review papers, most of them being devoted to alloying reactions. Based on this fact, it does not seem reasonable to plan an exhaustive historical review on this subject, but rather a specific one in order to setup a strategy for such a survey. The choice we made is rooted in the evolution of the studied anode materials and the progressive increase in knowledge and interest for simple systems rather than ternary or even more complex materials. Recently, there has been a change from studying rather complex systems, to studying relatively simple systems. It seems that the simplest systems are able to provide the most insight. Herein we present a review of some of these most important findings together with subsequent prospects.

In the early 70s, several groups1–3 demonstrated that alloying reactions of metallic lithium with metallic or semimetallic elements are electrochemically feasible at room temperature in a non-aqueous based electrolyte system with Li. Dey1 also pointed out that the alloys formed through this Spontaneous Electrochemical Alloying (SEA) are exactly the same as those metallurgically prepared. This is of first importance since it means that a lithium cell can be viewed as a way to electrochemically screen a Li–M phase diagram at room temperature. This last statement was recently contradicted by the formation of a crystallized Li15Si4 phase during the electrochemical lithiation of crystallized Si, a phase that is not predicted on the Li–Si phase diagram at ambient temperature.4 In ref. 1, one can also read “... the alloying caused complete disintegration of the electrodes and the consequent loss

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of electronic contact”. This sentence was a harbinger for the decades of research to come. Electrode pulverization as witnessed by these authors, and many others since then, is not unexpected when one considers a simplistic sketch based on the number of atoms lying within a single reacting particle. In contrast to a generic insertion process of Li-ions in an open oxide framework (MO₂ + Li LiMO₂) which comes with a 33% rise in the number of atoms, a dense metallic particle (such as Al) has to accommodate one Li per Al (Li + Al LiAl : 100% rise in the number of atoms). This effect is even more pronounced for Sn atoms in a Sn particle that must undergo a drastic “dilution” by a factor of more than 5 (4.4Li + Sn Li₄Sn : 440% rise in the number of atoms). These simple considerations are aimed at showing that the increase in the specific volume of electrode particles during a large alloying reaction is intrinsic to the process itself. Any attempt to reduce this change in volume will come with a limitation in capacity. Assuming a metallic state of Li, its atomic radius (2.05 Å) is far higher than those of the commonly studied host atoms (Sn: 1.72 Å, Si: 1.46 Å, Pb: 1.81 Å, Sb: 1.53 Å, Al: 1.82 Å). A lithiated particle always has a much larger radius than the original unliathed one. Barring significant changes in density, such large atomic uptakes will always result in high volume changes. It is important here to keep in mind that one of the most efficient electrochemical systems (Ni/Cd battery) is based on a Cd/(Cd(OH)₂) anodic redox couple, with a reaction implying 130% volume expansion. Despite these large volume changes, the electrode works fine and can sustain hundreds of cycles. A similar example is provided by the lead–acid system (the still most sold battery) working through PbO₂/PbSO₄ (50% volume change) and Pb/PbSO₄ (120% volume change) reactions. Highly reversible conversion reactions also come with huge volume changes, e.g. 100% calculated for the reaction Co₃O₄ + 8Li 3Co + 4Li₂O. These systems exemplify that the volumetric expansion is not limited to specific materials, and that new strategies are needed to address this challenge.

Fig. 1 Evolution in the number of papers related to anode materials for Li-ion batteries. Inset: overall repartition in journals, reviews and patents. Source: INIST.

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an absolute drawback and that electrode processing and additives are key issues.

Without doubt, the huge theoretical capacities linked to the formation of the Li-richest Li$_x$M binaries are very appealing for high-energy storage applications. The associated large energy densities support the present quest for good cycling behavior. This goal can be achieved by finding ways to limit (or even better eliminate) the loss of cohesion resulting from the alloying process, and by understanding the related textural modifications within both the active materials and the electrode itself.

Many approaches have been suggested and tested toward these goals, and some of them are worth being considered as important enough to be detailed. Here, we will try to illustrate each of these approaches by simple and recent examples.

This paper will be structured as follows: first, we will discuss the choice of the metal(s) we believe are worth focusing on by a compromise with various parameters such as electrochemical capacity, cost, voltage, toxicity, etc. Then, we will discuss the electrochemical performances of these materials as thin films and the best results to-date, in terms of capacity and capacity retention (sometimes at the expense of the active mass). To ensure maximal capacity the contribution of the inactive substrate or related additive must be minimized. This will be the subject of the next section where the various proposed strategies toward this goal will be compared. Finally, some alternative strategies and concepts will be proposed prior to the conclusions of this survey.

**Which metal(s) is(are) the best candidate(s)?**

Fig. 2 conveys some important messages in view of targeting the right elements to be studied. The Si data are calculated based on Li$_{3.75}$Si (Li$_{15}$Si$_4$). Keeping in mind that the abundance, cost and toxicity of the material/element (i.e. ecological concerns) of interest will sooner or later be at the centre of this debate, let’s start by selecting abundant, cheap and environmentally benign elements. First, in terms of gravimetric capacity, Si is far ahead of the other metals or metalloids, next is Al with 25% of the gravimetric capacity of Si. From this point of view, Si wins. Note that these two metals are by far the most abundant in the Earth’s crust. Now, in terms of volumetric capacity, the difference is less. While Si is still ahead with around 8500 Ah L$^{-1}$, Sn and Pb are not far behind with 65–75% of the Si capacity. Thus, owing to the user’s demands for alternative negative electrodes with both higher volumetric and gravimetric capacities than carbons, Sn and Si appear as the main elements to focus on. Note that each of the alloys presented in the chart has volumetric capacity of at least twice that of graphite.

**Elemental films**

Many groups have reported that amorphous Si films deposited on dense metallic substrate (e.g. Cu) have very good cycling efficiency when cycled down to 0.0 V vs. Li$^+$/Li$^-$ (Fig. 3 and 4). It was postulated that this excellent behavior is linked to the very good adhesion of the films onto the substrate which allows a constant pinning of the active material to the substrate and thus maintains the electrical contact. Literature shows that the first lithiation cycle induced an increase in the film thickness which was shown to be constrained in a direction perpendicular to the substrate. However, a curling of the films was occasionally observed during the reaction, suggesting the existence of important stress in the expanding material. The first Li removal is a formatting step with the

**Fig. 2** Gravimetric and volumetric capacities for selected alloying reactions. Capacities for graphite are given as references.

**Fig. 3** Transmission Electron Microscopy (TEM) picture, Selected Area Electron Diffraction (SAED) pattern and cycling performances of evaporated amorphous Si films deposited on Cu substrates. Cycling performances for Si nano-particles, bulk Si and graphite are given as references. Capacities are given per gram of active material (silicon, carbon). Reproduced by permission of ECS – The Electrochemical Society.
creation of large cracks within the films as a result of shrinking in both directions. There is a breathing of these “mud clusters”\(^{10}\) (Fig. 5) upon subsequent cycles.

The use of amorphous deposits is likely preferred in order to avoid any anisotropic expansion of oriented grains within the films during alloying. The volumetric expansion and the stress are so strong that a relatively thick substrate (i.e. large inactive mass) is required which reduces the overall capacity. In contrast, the use of thin substrates results in rapid pulverization of the films and complete capacity loss after a few cycles. Within this context, a recent investigation on Cu\(_2\)Sb supported films\(^{11}\) grown on various substrates is also of great interest, since it suggests that the better performances observed for Cu compared to stainless steel substrates are due to a better compatibility with the extruded copper. Thus, the nature of the substrate is not as transparent as it seems towards the reaction mechanism and therefore to the cyclability of the active deposit. The growth of a Li–Cu–Si phase at the interface of Si/Cu films upon cycling has been proposed as a probable origin for the progressive failure of the Si films.\(^7\)

It’s commonly accepted and now well documented that Si films can exhibit nice reversibility provided they are made amorphous (or rendered amorphous during the first cycle), and remain amorphous during the cycling.\(^5\)\(^{-10,12-14}\) Based on a simple stacking model, an amorphous metallic material always has a lower density than the dense crystallized form. Though, the gain in “free space” for Li atoms will be not enough to significantly reduce the extent of the volumetric changes during large Li uptake. However, the intrinsic absence of phase transitions and their isotropic expansion seems to have a very positive impact on their cycling performances. So far, no data can help in discriminating between the isotropic expansion and the absence of transition to account for this improvement. Nice reversibility and very high capacities have been reported for sub-micron Fe/Si multilayer films and for post-annealed films made of alternating Co/Si layers despite some degree of crystallization and textural modifications of the deposits.\(^{15,16}\) (Fig. 6).

These reports showing the high reversibility of the alloying reactions when active films are used have prompted intensive research and many approaches have been investigated to process powdered Si materials while preserving the superior cycling performance of thin films.

**Small domains**

Initiated by Yang *et al.*,\(^{17,18}\) the use of small domains has been deeply explored. It turned out that ductile elements such as Sn can be cycled as small reacting dots, provided that a matrix prevents its agglomeration.\(^{19,20}\) Otherwise, this would result in particle growth leading back to the inability to sustain the stress induced by alloying without loss of point contact. Such
an aspect, together with the need for limiting the side reactions with electrolytes at the surface of such small particles (high specific surface of contact), has triggered research on composite materials.

**Composites and matrixes**

Si nano-particles behave in a very promising manner when included in a conducting and dense matrix. This has been shown by numerous groups with Si/C and Sn/C mainly. The best performing Si/C composites are made from intimate Si/PVC mixtures pyrolyzed under argon, Fig. 7, and spray dried at 400 °C with Si/citric acid/ethanol suspensions Fig. 8. Sn/C composites of interest are prepared by infiltration of tin tetraethyl in porous resin, Fig. 9. Many aspects of the reactivity of these composites, however, are still not understood. For instance, it was observed by Raman spectroscopy, Fig. 10, that, when Si particles are embedded in a dense carbon matrix, a compressive force is applied to the Si particles. Even a mild manual grinding (pestle and mortar) of the micrometric particles of Si/C composites has a very negative impact on the cyclability, concomitantly observed with a relaxation of the pressure according to Raman studies, suggesting an important role of the tensile strength around the particles. Such a grinding step was shown to be successfully by-passed by casting the precursor slurry (Si dispersed in a PolyEthylene Oxide solution of PolyVinyl Chloride) as a film before pyrolysis. Therefore, questions remain regarding the role of the C coating. Does it limit the volume expansion or does it solely screen the surface of the Si particles and then expose the electrolyte to carbon, leading to a solid electrolyte interphase (SEI) whose properties are not detrimental to the cycling of the system? Surely, other materials such as borates and/or phosphate glasses can be used as matrix agents. The resulting electrode materials, however, display significant irreversible capacity during the first few cycles, although very good long-term capacity retention is obtained.

This concept of active particles trapped inside an inactive matrix can also be pushed forward by trapping active atoms in between inactive grains, at their boundaries. This was shown to be possible with Sn atoms located at the SnMn₃C grain boundaries and alloyed with Li, but no definitive answer was yet released regarding the exact localization of the active part that was ascertained to be Sn by a Mössbauer study. The
Fig. 6  Top, left: Transmission Electron Microscopy (TEM) cross-sectional image of a typical Co/Si multilayer film prepared by sequential electron-beam evaporation onto a copper substrate (a) as made and (b) after post-annealing at 350 °C for 30 min. Right: corresponding gravimetric capacity evolution as a function of cycle number.15 Bottom, left: Transmission Electron Microscopy (TEM) cross-sectional image of a typical Fe/Si multilayer film prepared by sequential electron-beam evaporation onto a copper substrate. Here, a pre-layer of Ti is used to improve adhesion. Right: gravimetric capacity evolution as a function of cycle number for various film thicknesses ranging from 755 Å (A) to 2455 Å (B) consisting of stacking of 95 Å thick Si and 75 Å thick Fe layers.16 Copyright Elsevier.

Fig. 7  Voltage vs. composition galvanostatic plots (right) and capacity evolution upon cycling (left) for nano-Si powder (<100 nm), nano-Si/carbon ex PVC composite (SPVC), and (nano-Si + Graphite)/carbon ex PVC composite (SGPVC).21 Reproduced by permission of ECS – The Electrochemical Society.
An interesting parallel can be drawn between these studies on binders and the recent demonstrations of the effect of carbon loading on the performance of physical Si/C mixtures. Recently, with a classical PVdF binder (10 wt%), a simple electrode prepared by mixing 20 wt% Si with 70 wt% graphite was indeed shown to present outstanding cycling efficiency (Fig. 13), stressing that almost full capacity of Si can be obtained and maintained for 150–200 cycles. The same group previously showed that Si/C composites prepared by chemical vapor deposition of Si at the surface of graphite particles also exhibit very good electrochemical properties, despite low (7%) Si loading (Fig. 14). These two examples are amongst the most appealing in the field of the Si/Li system, and again nicely exemplify that the simplest investigations often reveal the most important insights. These excellent results can be seen as originating from either the very good electrical wiring provided by the huge carbon content or the “space filling” matrix effect played by carbon. As a preliminary answer, our recent investigations on this aspect show that very similar results can be obtained with a high binder loading instead of a high carbon loading.

In situ amorphous/crystal transitions

Recently, Obrovac and Krause demonstrated that a limitation (Constant Current–Constant Voltage, CCCV) in discharge voltage (0.17 V vs. Li+/Li) of a bulk Si<sub>crystallized</sub>/Li cell can be efficient in limiting the amount of reacted Si. The non-reacted Si remains crystallized while the reacted part turns amorphous and remains amorphous during Li uptake and removal. Excellent cycling efficiency is then observed (900–1000 mAh g<sup>−1</sup>) over at least 100 cycles, provided that the right binder is used, a pre-conditioning cycling procedure and a voltage limitation applied (Fig. 16). This approach can be seen as the in situ creation of a non-reacted substrate (inner
crystallized Si) that limits the loss of integrity of the active part (surface reacting layer/film of Si). From a fundamental point of view, this strategy and this CCCV cycling limitation in voltage is elegant, but will be difficult to implement for real applications. Even if the role of the binder is not clearly established in this case, it still shows that very large crystallized Si particles can be nicely cycled. This suggests that nanomaterials are not mandatory, as early believed, to reach excellent performances. An additional key parameter seems to be again the right choice for the binder maintaining electrical contact between particles and with the current collector. Another interesting study by this group has revealed that a crystallized Li$_{15}$Si$_4$ phase is formed upon Li reaction with amorphous Li$_x$Si, for films thicker than 2 μm. This turns out to be an important finding, keeping in mind that materials which undergo drastic phase changes typically do not perform well.

**Solid solution vs. phases transitions**

The Li reaction with an amorphous and remaining amorphous material can be seen as solid solution behavior, without phase transition and with smooth evolution. Along that line, we are still waiting for the definite data/experiment showing that the loss of electrical contact between particles during lithium-alloying is due to either large volume changes, or associated with important structural stresses (i.e. phase transitions), or both of them concomitantly. So far, we cannot point a finger at one definitive cause and it is still claimed that the disconnection is important and results from the combined effects of both phenomena.

Two approaches can be envisaged to sort-out this dilemma: (1) find alloying reaction(s) coming with important phase transitions but limited volume changes (i.e. open metallic framework), or (2) alloying reaction(s) implying volume changes only, that is to say solid solution domains of alloying.

Unfortunately, to our knowledge, there is no Li–M binary system with such an open M framework allowing limited volume changes while Li content is increased. Interestingly, we know of such open metallic frameworks that can insert large amounts of hydrogen atoms instead of Li. This is the case for LaNi$_5$ that can host 6 H per formula unit (doubling the number of atoms per unit cell) with only 20% volume expansion. Finding equivalent host structures for Li would be a great leap. There is one system, Li–Mg (Fig. 17), which exhibits large solid solution domains and having pure Li as the end-member. The cubic cell parameter slightly varies with the wide Li-rich solid solution domain, while large variations in $a$ and $c$ values are observed in the narrow Mg-rich part. The Li + M → LiM reaction, despite similar crystallographic parameters for M and LiM, will still correspond to a large particle volume change (around 100%). With one system, we have therefore the three situations in one: biphasic, monophasic with small changes in cell parameters, and monophasic with large changes in cell parameters. Despite these unique features, the Li–Mg system has been the subject of only a few papers and reports, the main reasons arising from the difficulties in preparing homogeneous materials, very low...
voltage vs. Li$^+/\text{Li}^0$ and very inhomogeneous Li-diffusion resulting in non-homogeneous (de)alloying processes and non-equilibrium phase compositions. Based on a recent paper,\textsuperscript{43} this seems to have been by-passed by using ball-milled Mg/C composites that lead to quite stable capacity at very low voltages and a relatively high rate. Despite this interesting result, no data is presented regarding the impact on the cycling efficiency of the localization of the cycled Li range in the phase diagram. It is unfortunate, as there are many things to learn about this system that to some extent mimic the transition-free expansion of amorphous materials.

Aside from elemental matrices, AuNi$_2$Sn$_4$ has been proposed as a host material showing no cell parameter evolution while accommodating large amounts of Li.\textsuperscript{45} Therefore, this example was not so conclusive since its reversibility was found to be very poor. This can originate from many factors, depending on the reaction process itself (e.g. metal extrusion), and this appears as a key point when one deals with larger than two-element systems, as detailed later. Ni$_2$MnSb\textsuperscript{46} was shown to react with Li through a solid solution but no subsequent work has been done to confirm this point.

**Thermodynamic aspects – liquid metals**

It’s well known that a inter(sur)face has a positive free energy of formation, implying that what we consider as the bulk state is no longer under control when the size is reduced. In contrast to thermal conversion associated with variations in enthalpy, the energy stored and released in primary/secondary batteries is associated with variations in free energy. The free energy of the surface can be as large as tens of kJ mole$^{-1}$,\textsuperscript{47} and is not only dependent on the “amount” of interface, but also highly

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Fig. 10  Left panels: voltage-composition galvanostatic curves vs. Li for nano-Si (10–100 nm, Si$_N$), annealed Si$_N$ at 900 °C (50 wt% Ketjen Black, 1 Li/30 h, 20 °C), Si$_N$/C composite prepared by pyrolysis of a Si$_N$/PVC blend at 900 °C under N$_2$, and manually ground Si$_N$/C composite (56 wt% ex PVC carbon, 1 Li/10 h, 20 °C). Capacities are given by weight of (Si + C) composites. The equivalent contribution of the Ketjen Black KJ conducting carbon was computed and superimposed (bold dashed) to visualize its contribution to the overall capacity. Insets: Discharge capacity as a function of cycle number. Middle and right panels: Selected Raman spectra and mapping of the Raman signal over 20 μm × 20 μm areas.\textsuperscript{24}
dependent on the nature of the solid and its surrounding. Therefore, for a constant size of reacting domains, a simple change in composition can result in large changes in free energy, maybe accounting for the large polarization often observed in nano-systems. Also, the change in particle size during reaction with lithium has never been attempted to be correlated with this polarization. Along that line, the study of the surface energetic aspects linked to the coalescence of small particles (e.g. Sn) can give us important data to master and design new structures with minimum dead mass and/or dead volume.

Maintaining very small particles trapped in a matrix can give us the opportunity to create new reacting systems. At very small size and with appropriate metal/substrate combinations, the melting point depression of metals can lead to molten reacting domains within solid matrixes. Here, no phase

![Fig. 11](image1.png) Gravimetric capacities as a function of cycle number, measured between 0.02 and 1.2 V vs. Li⁺/Li⁺ for composite materials prepared by ball-milling of Si : SiC (1 : 2 mol ratio) (top) and Si : TiB₂ (40% mol Si) (bottom) mixtures, and for different milling times. Electrodes contain ca. 7 wt% of conducting carbon and ca. 6 wt% PVdF binder. Reproduced by permission of ECS – The Electrochemical Society. Copyright Elsevier.

![Fig. 12](image2.png) Left: voltage vs. composition galvanostatic plot (vs. Li⁺) for electrodeposited Sb/Sb₂O₃ coating (C/10). Right: gravimetric capacity as a function of the cycle number (C/10) for pure Sb deposit (squares) and for Sb/Sb₂O₃ coating. The coating contains 21 wt% oxide. Reprinted with permission from ref. 30. Copyright 2007 American Chemical Society.

![Fig. 13](image3.png) Scanning Electron Microscopy (SEM) image of the Si/Graphite composite electrode and corresponding cycling performances (per gram of Si + C) collected between 0.005 and 1.0 V vs. Li⁺/Li⁺. The electrode contains 20 wt% Si, 70 wt% graphite and 10 wt% polyvinylidene difluoride (PVdF) binder. Reproduced by permission of The Royal Society of Chemistry.
transition or electrical contact loss would hold any more. The recent report on the activity of the Li/Ga (Ga melting point under atmospheric pressure: 30 °C) system \(^4^8\) and its high

Fig. 14 Scanning Electron Microscopy (SEM) image of the Si/graphite composite electrode showing 10–20 nm Si particles. Cycling performances (per gram of Si) collected between 0.005 and 1.0 V vs. Li\(^+/\)Li\(^-\) in CCCV (Constant Current–Constant Voltage) mode. The electrode contains 90 wt% of Si/C active part and 10 wt% PVdF binder. The active part is made of 7 wt% nano-Si chemically vapour deposited from SiH\(_4\) directly on the surface of graphite (93 wt%). \(^3^5\) Reproduced by permission of ECS – The Electrochemical Society.

Fig. 15 Capacity evolution as a function of the cycle number for high carbon loaded\(^3^5\) and high CMC binder loaded\(^5^6\) Si-containing electrodes. Reproduced by permission of ECS – The Electrochemical Society.

Fig. 16 Voltage vs. composition plot for a Si/Li cell undergoing preconditioning cycles and CCCV cycling as described in ref. 37 and corresponding capacity (circles)/coulombic efficiency (cross) as a function of the cycle number. Reproduced by permission of ECS – The Electrochemical Society.

Fig. 17 Binary Li–Mg phase diagram.
volumetric capacity (4500 Ah mL⁻¹) make it conceivable as a model for such investigation (Fig. 18).

The alloying reactions in Li–M binary systems being bound to the free energy of formation of the LiₓM phases, mastering the control of the cell potential is only possible by playing with the choice of M and, to some extent, of the size of the reacting domains (provided theoretical and thermodynamical data are available). Moving to binary, ternary of even more complex systems, this point seems to be less out of control.

Multi-element metallic materials

Beyond the scope of this paper mainly dealing with pure metals/elements, these multi-element materials are generally randomly scrutinized and the subject of many papers. From a practical point of view, they provide new degrees of freedom in selecting the desired potential of reaction with lithium.⁴⁹ The tunable parameters are multiple: the nature and the number of the metals themselves, their stoichiometry in the alloy, the choice of metals that alloy with lithium, or not; possible different structural forms, etc. If we also consider the effect of particle size, crystallization state, and cycling parameters, the difficulties quickly appear in extracting some general conclusions from this class of materials and related publications.

Basically, all the approaches described above can be applied to these multi-metallic systems, with similar drastic improvements. For instance, the cycling efficiency of Cu₂Sb/Li cells has been recently improved by making powdered Cu₂Sb/C via PVC decomposition composites.⁵⁰

The main difference between these systems and the Li–M binaries is the ways the volume expansion is expressed and how it can be less detrimental to the cycling efficiency. When Li reacts with M, only Li–M can form. In contrast, when Li reacts with appropriate MN binary, the uptake of Li can be compensated by the extrusion of N concomitant to the formation of Li–M binaries. This extrusion can take different aspects (amorphous, crystallized, dendrites) but it generally seems to be an efficient way to accommodate the excess volume occupied by Li atoms.¹¹,¹⁷,¹⁸,⁴⁶,⁵¹–⁵⁷ The dead mass/volume carried by the N part is generally righting acting as a buffer but also in some cases as a limitation to the reaction along long-term cycling. This was shown for the Sn–Fe–C system with growth of an Fe layer (detected by Mössbauer) that hinders the Sn particles from reaction with Li atoms.⁵⁸

The selection of the N elements could be driven by such agglomeration considerations. The initial MN alloys can be recovered at the end of the charge but other crystallographic forms or new Li–M–N ternaries are reported.

Which strategy to be picked up? Next steps

The drawback for all these strategies is the lowering of the capacity due to the use of substrates (dense films, limited reaction), voids (porous powders), matrices (grain boundaries, composites materials, high carbon loads), and binders. These extraneous components are all inactive or kept non-reacted, therefore giving much less capacity than theoretically. Each of these concepts, aiming towards fighting the problems due to the volumetric expansion, led to lower gravimetric and volumetric capacities. Thanks to this arsenal of electrode design strategies, we are now able to cycle metals versus metallic lithium and to reach theoretical capacity.

Tracking back the history of implementation of carbonaceous materials in Li-ion cells, the problems and selection rules we will have to now address are those of safety, mechanical stability, cycling at various temperatures, and final cost resulting from the processing of the active material. As performed for carbonaceous materials, thermal studies of the lithiated metallic electrodes have to be planned, but this task will be complicated by the numerous possible interactions within these multi-member systems: active material + solvent + salt + buffer (+ additives). The simple Si/C mixtures proposed by Holzapfel et al.³⁴,³⁵ are from this point of view the simplest systems to be studied. Recent experiments indicate that Li, Si alloys are much safer towards electrolyte reaction than graphite, for the same Li contents,⁵⁹ but no data is available about the reactivity of, for instance, new carbon-based binders during thermal runaways: CMC for example, since cellulose is a carbohydrate polymer, one can forecasts its high reactivity.

Conclusions

Through this review we hope to have conveyed the message that the practical utilization of electrodes, whose volume can reversibly change by more than 300% upon cycling, is not an
easy task. Therefore, recent advances have indicated that we have come a long way so that 50 to 100 cycles can now be achieved by a few groups. The approaches have been somewhat different enlisting either the use of (1) single element alloys (Si, Sn) embedded in carbon whose role is twofold by providing electronic conductivity together with pressure confinement, (2) binary Si or Sn-based alloy M,Sn(Si)/C composites that through the first reduction process lead to a nanocomposite made of electrochemically active species (Li,Sn, Li,Si) surrounded by a non-electrochemical active “3d-metal” M. The latter has led to the commercialization of the Nexelion battery based on a carbon negative electrode highly loaded with a Co–Sn-based material, and leading to an overall gain in volumetric energy of 25%. Nevertheless, whatever the approaches used, the proper functioning of such electrodes lies in their confection, which is governed by means to limit the overall electrode expansion together with metal particle migrations upon cycling. A critical survey of the presented data indicates that somewhat similar performances can be achieved by either (1) electrical means such as limiting the values of inserted Li (x) in Li,M upon cycling so as to limit the electrode expansion, (2) chemical means through carbon coatings that maintain the alloy particle under stress limiting to a certain extent this expansion and (3) by playing with the electrode formulation, namely with the ratio of electrochemically active material to carbon additive or binders, not in excess of 25% so as to have an electrode with limited volume expansion. Along that line, the advantages of using a binary vs. a single alloy element is still questionable; therefore a foreseeable advantage with the former is that, for instance, upon cycling the oxidized Li,Sn phase apparently reacts with Co to form again nano-“Li,CoSn2” preventing coarsening.\(^5^3\) For the latter, the formed Sn particles can have a tendency to agglomerate to decrease their surface energy if not nicely confined in their host C or binder matrices, leading then to poor performance. Now, a legitimate question remains regarding the possibility to prepare electrodes based on alloying reactions that could be utilized in terms of energy density without losing their overall performance. Moving from bulk electrodes to thin film electrodes provides an answer to this question, namely in terms of capacity retention, with therefore a price to be paid in terms of overall energy density. Needless to say that moving to expanded or nano-architected electrodes can recover part of the electrode energy density with therefore a non negligible additional cost. Moving from bulk to nanoparticles (either crystallized or amorphous), which are more stress-free upon Li insertion, have resulted in performance improvements but certainly not worth endorsing the cost of downsizing the particles. Thus, research breakthroughs still need to occur prior to taking full advantage of such alloying reactions. The chances of succeeding may still reside in getting a better understanding of the fundamentals governing such alloying reactions since, for instance, the first basic question of whether a single-phase vs. a two-phase Li-alloying process is better for electrode performance is not yet known. Along that line the study of Li-based Mg alloys could be essential as such systems show a wide range of solid solutions. The future of this field may also depend on advances in analytical instrumentation as it is becoming critical to study nano-scale effects. For instance, Sn–Fe–C and Sn–Mn–C perovskite phases were shown to exhibit surprisingly sustained low reversible capacities postulating to arise from grain boundaries, but never irrevocably confirmed. Besides, while intense research is devoted to physically made composite electrodes (mechanical milling) or chemically made (impregnation, pyrolysis) electrodes, little effort is put aside to chemically structured composites, that is to say open highly porous framework structures whose pores could, for instance, serve as chemical reactors to generate in an \textit{in situ} manner confined metal nanoparticles. Some of these approaches are being presently pursued within the ALISTORE network with interesting preliminary results.

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