

Secondary Lithium-Ion Battery Anodes: From First Commercial Batteries to Recent Research Activities

Addressing the challenges in rechargeable lithium-ion battery technologies

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Following the development of commercial secondary lithium-ion batteries (LIBs), this article illustrates the progress of therein-utilised anode materials from the first successful commercialisation to recent research activities. First, early scientific achievements and industrial developments in the field of LIBs, which enabled the remarkable evolution within the last 20 years of this class of batteries, are reviewed. Afterwards, the characteristics of state-of-the-art commercially available anode materials are highlighted with a particular focus on their lithium storage mechanism. Finally, a new class of anode active materials exhibiting a different storage mechanism, namely combined conversion and alloying, is described, which might successfully address the challenges and issues lithium-ion battery anodes are currently facing.

1. Introduction

Rechargeable (i.e. secondary) LIBs are now our everyday companions, powering our laptops, cellular phones, tablets, portable audio players, etc. Due to their high specific energy, superior coulombic efficiency and outstanding cycle life compared to earlier battery systems like lead-acid, nickel cadmium or nickel metal hydride (1), LIBs quickly conquered the battery market for consumer electronics (2) and are at present the power source of choice for these applications (3). In view of limited crude oil resources and climate endangering emissions (e.g. CO₂) deriving from the consumption of fossil fuels, LIB technology is currently facing a new great challenge: its implementation in large-scale devices like (hybrid) electric vehicles and stationary energy storage to balance the intermittent supply of renewable energy sources such as wind, solar and tidal (3–5). Although some electric and hybrid vehicles are now becoming available, the energy density of LIBs still needs to be substantially increased by a factor of two to five compared to the existing state-of-the-art technology (150 Wh kg⁻¹) to push these vehicles out of the niche market sector, paving the way for a fully sustainable transportation system (6). However, the conversion of electrical energy to chemical energy (and *vice versa*), corresponding to the charge (and discharge) of a LIB, is a complicated process due to the various participating components in a lithium-ion cell, their (electro-)chemical properties and their extensive interdependencies (4).

Generally, LIBs are built of two electrodes (anode and cathode), separated by an electrically insulating though ionically conducting liquid electrolyte supported on a porous separator to ensure the transfer of charge carriers (lithium-ions) from one electrode to the other (7, 8). It appears noteworthy that the separator-electrolyte system may also consist of a non-porous polymer layer, i.e. a solid-state polymer electrolyte (SPE) membrane, occasionally swollen by a liquid electrolyte, i.e. a gel polymer electrolyte (GPE) (9). A deep understanding of the chemical and electrochemical interactions of these components throughout the lifetime of a LIB is certainly crucial to develop new concepts for advanced lithium-based battery technologies in future (3). However, in a first step each component of the cell has to be addressed solely, keeping the other cell parameters constant.

This article reviews the development of lithium-ion anode materials (**Section 2**), focusing initially on those materials that were or are already employed in commercial batteries (**Section 3**). Subsequently, promising alternatives for these currently utilised anode materials are briefly reviewed, in particular those materials storing lithium by a combined alloying and conversion mechanism (**Section 4**). Interdependencies of these lithium-ion anode materials and other cell components are also addressed.

2. The Development of Commercial Secondary Lithium-Ion Batteries

The most elementary anode material for lithium-based batteries is obviously metallic lithium, which has been used for primary (i.e. non-rechargeable) batteries since the early 1960s (10, 11). By possessing the lowest standard potential (-3.05 V vs. a standard hydrogen electrode (SHE) (12)) and the lowest atomic weight (6.94 g mol⁻¹; specific gravity: $\rho = 0.53$ g cm⁻³) among all metals, the utilisation of metallic lithium as an anode offers the realisation of galvanostatic cells having an extremely high energy density (10, 13, 14). Consequently, metallic lithium was also considered the candidate of choice for secondary lithium-based batteries (10, 15, 16). However, lithium metal cells have one severe drawback, namely, inhomogeneous lithium plating, which halted their commercial development three decades ago. This uneven deposition of lithium onto the anode surface upon charge results in the formation of so-called dendrites (11, 17, 18). These dendrites consist of high surface area, highly branched

lithium metal structures, which continuously grow, eventually penetrate the separator and electrically connect the anode and cathode leading to a short circuit of the cell. This spontaneous and uncontrolled event results in local heat evolution and – in the most unfortunate case – thermal runaway of the cell (19, 20).

To circumvent this severe safety issue, in the 1970s several researchers developed the concept of lithium-ion host structures, later commonly named insertion compounds, thus avoiding the risk of superficial (dendritic) lithium growth (21–24). In the course of these developments Scrosati and Lazzari proposed the ‘rocking chair battery’, which marked the first practical realisation of two host materials reversibly shuttling lithium-ions from the anode to the cathode upon discharge and *vice versa* upon charge (7, 8). Nowadays, all commercially available secondary LIBs make use of this concept, although they employ different active materials as cathode and anode.

Regarding the anode side, carbonaceous materials are generally used as the lithium-ion host framework (10, 11). The first commercial secondary LIB, released by Sony Corporation in 1991, comprised LiCoO₂ as cathode and a soft carbon (more precisely coke; soft carbons can be graphitised by thermal treatment at about 2300°C) as an anode (**Figure 1**). This LIB provided an energy density and specific energy of 200 Wh l⁻¹ and 80 Wh kg⁻¹, respectively, outperforming all other battery technologies present in the market at that time. Moreover, this battery showed a highly reversible and stable cycling behaviour and an extremely high cell voltage of about 4 V, employing propylene carbonate (PC) as electrolyte solvent (10, 15). The replacement of soft carbon by hard carbon (**Figure 1**) (i.e. non-graphitisable carbon), offering enhanced specific capacities, led to an increase of the achievable volumetric and gravimetric energy density up to 295 Wh l⁻¹ and 120 Wh kg⁻¹, respectively (10, 15). The hard carbon anode facilitated the increase of the upper cut-off potential to 4.2 V, while presenting excellent cyclability in the – at that time – commonly used PC-based electrolytes (10, 15).

In summary, it can be stated that (by carefully controlling the heat treatment temperature) hard and soft carbons can be obtained, providing acceptable specific capacities, low initial irreversible charge loss and relatively low (dis-)charge hysteresis, enabling efficient energy conversion and storage (25, 26). Nevertheless, the desired application of LIBs in cellular phones required the replacement of such anode

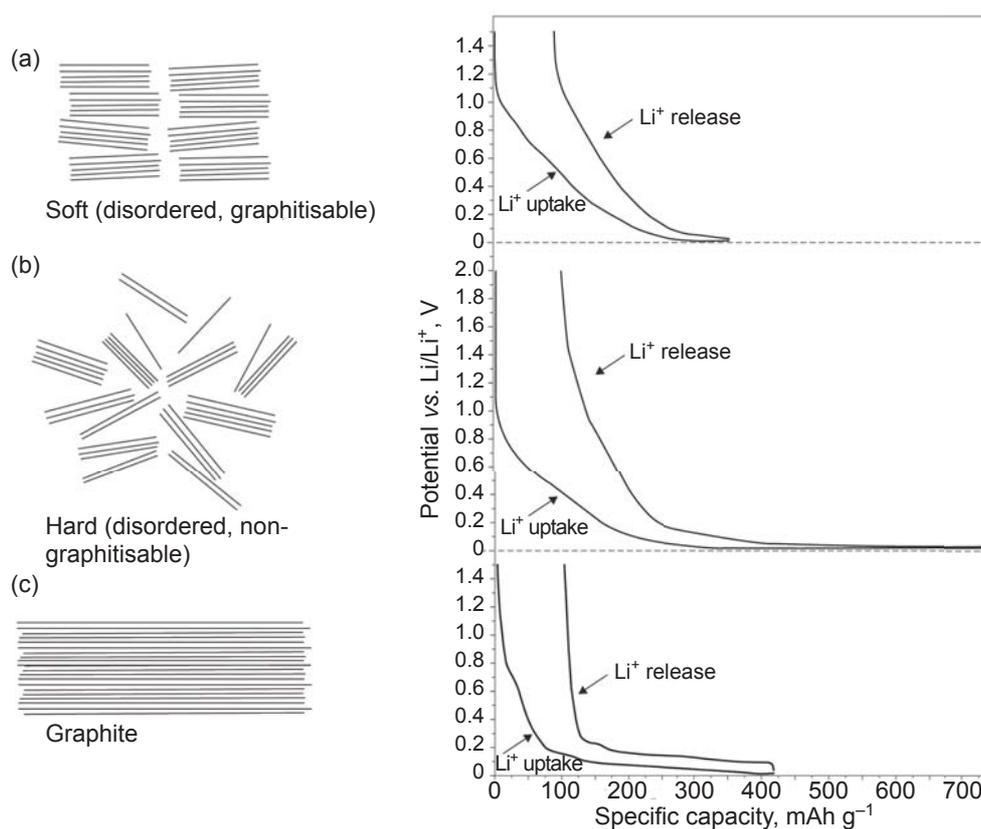


Fig. 1. Schematic illustration (left side) of: (a) soft carbon; (b) hard carbon; and (c) graphite structures and (right side) their typical potential profiles (Figure redrawn from (15, 16))

materials, as the voltage drop in the potential profile of both carbonaceous materials (13) upon (dis-)charge (Figure 1) results in a substantially varying overall cell voltage. However, cellular phones need an operational voltage of at least 3 V (27). In addition, the utilisation of these anode materials suffered a severe safety issue. In order to achieve the maximum specific capacity, the cathodic cut-off potential (i.e. the end-of-charge potential for the anode) must be set close to 0 V vs. Li/Li⁺ (16), thus, again posing the risk of metallic – in worst case dendritic – lithium plating on the carbon particles surface. For these reasons a new anode material was required. Graphite advantageously addresses all these issues rather satisfactorily and is thus still the most commonly employed anode material in today's commercial LIBs (5).

3. State-of-the-art Lithium-Ion Battery Anode Materials

3.1. Graphite

In contrast to soft and hard carbons, graphite shows a rather flat potential profile when reversibly hosting

lithium-ions at potentials below 0.5 V vs. Li/Li⁺ (Figure 1) (25, 28, 29). Additionally, it offers a significantly higher specific capacity of 372 mAh g⁻¹ (corresponding to one lithium per hexagonal carbon ring, i.e. LiC₆) with limited irreversible capacity (10, 13, 15). Graphite is composed of graphene layers, stacked in AB or ABC sequence and held together by van der Waals forces (13). Upon (dis-)charge lithium-ions (de-)intercalate into the layered structure by a so-called staging mechanism, resulting in an AA stacking configuration once it is fully lithiated (25, 28, 29). Another great advantage of graphite is its high electronic conductivity, originating from the sp²-hybridisation (*p*-orbitals building a delocalised electron network) of the carbon atoms located in the planar, hexagonally structured graphene layers (13).

A major obstacle for the implementation of graphite-based anodes, however, was their incompatibility with the standard electrolyte solvent PC (10, 15). In 1970, Dey and Sullivan observed the electrochemically induced degradation of the graphite structure in PC-based electrolytes (30). As reported in later studies, the reason for this degradation was the co-intercalation of solvent molecules, i.e. the solvation shell of the

lithium-ions in the electrolyte, leading to a volume expansion of ~150% and subsequent exfoliation of the single graphene layers (13). Furthermore, lithium-ion intercalation occurs at potentials beyond the electrochemical stability window of common electrolytes. Therefore, a continuous reductive decomposition of the electrolyte components takes place, leading to a drying-out of the cell and hence a rapid capacity fading. The implementation of graphite as lithium-ion anode was made possible, finally, by replacing PC with mixtures of short-chain linear alkyl carbonates (low viscosity) and – most importantly – ethylene carbonate (EC, high dielectric constant (28)). These solvents are also not stable (thermodynamically) at such low potentials, but the initial decomposition of EC results in the formation of a stable, electronically insulating, ionically conductive film on the graphite particles surface, preventing direct contact of the active material and the electrolyte while at the same time inhibiting the co-intercalation of solvent molecules (Figure 2) (17, 18, 28, 29, 31, 32). Following an early study by Peled, this protective surface film is now known as the solid electrolyte interphase (SEI) (31).

The replacement of hard carbon by graphite as an anode led to a further jump in volumetric and gravimetric energy density up to 400 Wh l⁻¹ and 165 Wh kg⁻¹, respectively (10, 15). As the theoretical capacity of graphite has now been mostly achieved, recent research efforts to further improve the performance of LIBs are basically dedicated to minimising the first cycle irreversible capacity, for instance by modifying the graphite surface. An extensive description of these research activities is certainly beyond the scope of this review and the interested reader is referred to Bresser

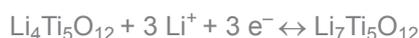
et al. (27) (and references cited therein), who provide a more detailed overview on this subject.

As mentioned earlier, graphite is still the most used anode material in commercial LIBs. However, as with soft and hard carbons, it entails the inherent risk of metallic lithium plating, an intrinsically limited high rate capability upon charge and a very high reactivity towards the electrolyte in the lithiated state, which might result in thermal runaway and occasionally the event of a fire if the SEI gets damaged or decomposes due to the overall temperature of the cell exceeding 130°C (11, 17, 18, 33–37).

3.2. Lithium Titanate, Li₄Ti₅O₁₂

A very promising alternative for graphite is spinel-structured Li₄Ti₅O₁₂ (LTO), which was first reported in 1994 (38). The reversible (de-)insertion of Li⁺ in the LTO framework occurs at a comparably high potential (about 1.55 V vs. Li/Li⁺) and the theoretical specific capacity is relatively low (175 mAh g⁻¹). Consequently, the achievable energy density of a lithium-ion cell employing LTO is much lower compared to graphite-based cells (38–40). However, LTO exhibits several great advantages compared to graphite, resulting in steadily growing interest regarding its commercial application (41–43). While the rather high operating potential of LTO certainly restricts the overall energy density, it allows the realisation of inherently safer LIBs. Since common electrolytes are thermodynamically stable at 1.55 V vs. Li/Li⁺, no vigorous electrolyte decomposition occurs, thus avoiding issues related to the growth or breakdown of the SEI. The operating potential is far from the region where metallic lithium plates onto the anode surface and consequently no dendritic formation can occur (34, 38, 39, 42, 44). In addition, the negligible volume expansion (39, 45) of LTO upon (de-)lithiation results in an outstanding cycling stability for more than tens of thousands of fast (dis-)charge cycles (46, 47).

As apparent from Figure 3, LTO exhibits a desirable flat potential profile corresponding to a two-phase (spinel to rock-salt) electrochemical lithium (de-)insertion process (48):



The insulating character (49) of spinel phase LTO, however, is a major obstacle for fast (de-)lithiation processes. Hence, several strategies were pursued to improve its electronic conductivity. *Inter alia*, nanostructuring of the LTO particles leading to shorter

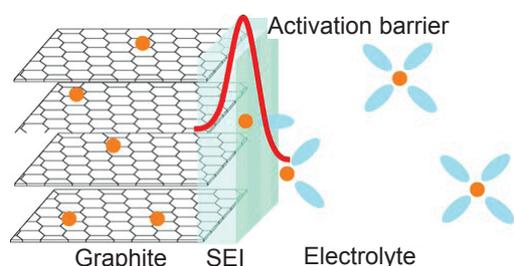


Fig. 2. Schematic illustration of the SEI on graphite, emphasising its role in the desolvation process of lithium ions prior to the intercalation of lithium into the graphite host material (Reproduced with permission from (32). Copyright 2009 American Chemical Society)

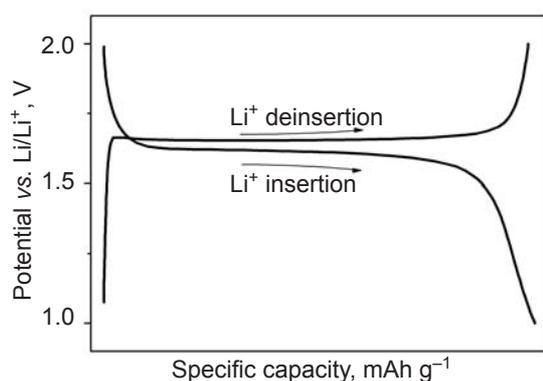


Fig. 3. Typical potential profile for a LTO electrode showing a flat Li^+ (de-)insertion plateau and a low voltage hysteresis (Image courtesy of Guk Tae Kim, Helmholtz Institute Ulm (HIU), Ulm, Germany)

diffusion pathways for lithium-ions and electrons and an increased electrode/electrolyte contact area resulted in a remarkable enhancement of its electrochemical performance, particularly at high (dis-)charge rates (14, 44, 47, 50). Further improvement was achieved by coating the (nanosized) particles with conductive surface layers (e.g. carbon) or by introducing LTO in highly conductive mesoporous (carbonaceous) matrices (48, 50–52). As a result, LTO appears highly attractive for the realisation of substantially safer, high power LIBs (5, 45, 53).

3.3. Alloying Materials

Several elements (e.g. Sn, Pb, Al, Sb, Zn, Si) are able to reversibly form alloys with lithium at low potential (54, 55). In contrast to the already discussed lithium storage by intercalation and insertion, the alloying mechanism is fundamentally different, giving rise to multiple new issues. However, with appealing theoretical specific capacities (exceeding that of graphite up to tenfold) and hence, energy densities, alloying anodic materials are currently intensely researched (56–58). Clearly, one of the major issues regarding alloying materials in general is the large volume expansion/contraction upon (de-)lithiation, leading to the fracturing of active material particles, the subsequent loss of electronic contact and finally the pulverization of the electrode (57, 59).

More than ten years ago an amorphous tin-oxygen-based composite was developed by Fuji Photo Film Corporation (60). However, it has never been successfully commercialised for various reasons. Upon

initial lithiation, in a partially irreversible step, Li_2O and metallic Sn are formed, followed by a reversible alloying reaction of lithium and tin (61). It was assumed that the electrochemically inert ‘matrix’ of Li_2O separating the initially formed tin nanograins would prevent the latter from aggregation upon cycling (62, 63), but not least due to the substantial volume expansion of ~200% (56) accompanying the alloying reaction, the comprised tin still aggregates upon long-term cycling (64, 65). This leads to rather rapid capacity fading after several cycles.

Therefore, research efforts were focused on creating secondary particle structures or matrices which are capable of buffering this volume expansion/contraction stress. Such research efforts comprised *inter alia* the preparation of hollow carbon nanospheres (66), core-shell nanostructures (67–69) and submicron- or micron-sized carbonaceous matrices (70–73). Despite these very promising approaches, to date only one tin-based alloying material – a composite of tin, cobalt and carbon – has been successfully employed in commercial LIBs (56, 74). It is reported that upon lithiation this Sn-Co-C composite initially forms a Li-Sn-Co phase, which subsequently separates into a Li-Sn alloy (75) and amorphous cobalt, provided that a sufficient amount of cobalt is present in the initial composite (76). Upon discharge, the delithiated tin alloys with the amorphous cobalt. This rather complex mechanism is supposedly the origin of the improved cycle life compared to pure Sn- or SnO_2 -based anodes (77–80).

It may be noted that very recently silicon-based anodes (more precisely, carbon-coated silicon nanostructures) were commercialised, promising substantially higher specific energies (81, 82) compared to pure graphite or graphite-based anodes containing a relatively low content of silicon (83).

4. Anode Materials for Next-generation Lithium-Ion Batteries

Research activities for the next generation of lithium-ion anodes are now focusing on the development of materials capable of surpassing graphite anodes in terms of energy, power and safety, while maintaining (if not improving) the level of environmental friendliness and raw material availability. Presently, nanosized alternative active materials (5, 84, 85) reversibly hosting lithium by both mechanisms discussed so far, insertion (e.g. N-doped carbonaceous materials or titanium

dioxide) as well as alloying (e.g. silicon or silicon oxide), are attracting world-wide scientific interest (27) and several excellent reviews are available for these very promising anode materials (44, 84, 86, 87).

In this review we focus on the latest upcoming research area characterised by a completely different lithium storage mechanism: chemical displacement or so-called conversion reactions.

4.1. Conversion Materials

Initially, displacement (i.e. conversion) reactions were considered to be irreversible at room temperature due to the extensive energy demand for bond breakage, atomic reorganisation, and the formation of new bonds (24). In 2000, Poizot *et al.* (86) reported for the first time reversible lithium storage using transition metal oxides as active materials, providing specific capacities of more than 700 mAh g⁻¹. Since then a growing interest in battery materials following a conversion mechanism (Figure 4) (88) can be noted, including transition metal oxides, sulfides, nitrides, phosphides, fluorides and other phases (89). The conversion mechanism can be generally described as follows (85):



Upon lithiation the transition metal (TM) is reduced to its metallic state and embedded in the simultaneously formed lithium-comprising compound Li_zA_y (where A stands for O, N, P, F and others). Due to the inherent physico-chemical properties of the initially formed TM nanograins, the formation of Li_zA_y becomes reversible (86). It might be noted that very recently also the reversible formation of lithium silicate, starting from cobalt silicate, was reported (90). Nevertheless, despite the growing knowledge about nanosized materials there is still a lack of fundamental understanding of the processes occurring in conversion materials, boosting the scientific interest regarding this class of materials (56). Commonly, nanostructured materials benefit

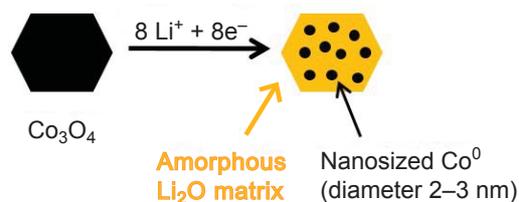


Fig. 4. Schematic illustration of the conversion mechanism shown exemplarily for spinel cobalt oxide (Figure redrawn from (88))

from enhanced electron and lithium-ion transport due to shorter diffusion (or more generally transport) pathways and reduced internal stress during volume expansion/contraction upon (de-)lithiation (56). For a more detailed insight into the (dis)advantages arising from using nanostructured materials for LIB applications the interested reader is referred to Bruce *et al.* (84), Scrosati *et al.* (74), Lee and Cho (87), and more recently Bresser *et al.* (91). Definitely, the most appealing feature of conversion materials is their ability to store more equivalents of lithium (two to eight per unit formula of the starting material) than any insertion compound (up to two), resulting in substantially higher specific capacities as displayed in Table I (3, 14).

However, conversion materials exhibit a series of severe drawbacks which necessarily need to be overcome before they can be seriously considered for commercial applications (89). The conversion reaction inherently causes a massive structural reorganisation, which potentially leads to a loss of electrical contact and electrode pulverisation (89). Moreover, conversion materials suffer from a very high reactivity towards commonly used electrolytes and a marked (dis-)charge voltage hysteresis, considerably affecting the energy storage efficiency of such electrodes (14, 89, 92). The elevated operational potentials of many conversion materials also limit the achievable energy density (14, 56) and the large first-cycle irreversible capacity is unacceptable for practical applications and requires special electrode treatments for compensation (56, 89). Taking into account the surface area which is frequently high (an intrinsic feature of nanostructured particles) and, as already mentioned, reactive, as well as the SEI instability known from compounds

Table I Comparison of Theoretical Specific Capacities of Selected Insertion and Conversion Materials^a

Material type	Anode material	Theoretical capacity, mAh g ⁻¹
Insertion	Soft carbons	200–1000
	Hard carbons	200–600
	Graphite	300–375
	LTO	175
	TiO ₂	330
Conversion	Metal oxides	500–1200
	Metal phosphides, sulfides or nitrides	500–1800

^aTable prepared according to (13, 85)

experiencing considerable volume changes (56, 86), conversion materials have just reached the early stage of development. For a detailed summary concerning the different types of conversion materials the interested reader is referred to Cabana *et al.* (89), Nitta and Yushin (56) or Goriparti *et al.* (85).

4.2. Conversion-Alloying Materials

Conversion-alloying materials mark another step forward in developing high energy and high power lithium-ion anode materials. The idea behind this new class of active materials is to further increase the uptake of lithium per unit formula of starting material by using mixed metal oxides in which one of the comprised metals can further alloy with lithium after being initially reduced to the metallic state (93, 94). This obviously results in higher specific capacities than theoretically achievable for 'pure' conversion materials. Exploiting, for instance, the lithium alloying capability of zinc, iron is partially substituted by zinc in the commonly known conversion material Fe_3O_4 , giving e.g. ZnFe_2O_4 . Upon lithiation metallic zinc and iron are formed. Subsequently, zinc can further reversibly alloy with lithium. Overall, nine equivalents of lithium per unit formula can be stored in ZnFe_2O_4 (theoretical specific capacity: $1000.5 \text{ mAh g}^{-1}$) compared to only eight equivalents of lithium per unit formula in Fe_3O_4 (926 mAh g^{-1}) (94).

Analogously to other conversion materials, the chemical reaction of spinel-structured zinc ferrite and lithium, first reported in 1986 (95), was initially considered to be irreversible. Nevertheless, after conclusive proof of reversible lithium uptake in ZnFe_2O_4 thin films in 2004 (96), research efforts were focused on achieving high reversibility and increased specific capacities. Early studies nonetheless obtained neither stable cycling performance nor the material's theoretical capacity. Additionally, the rate performance, i.e. the achievable specific capacity at elevated specific currents, remained a severe issue (97–101). The apparently inevitable capacity fading was attributed to the formation of an insulating polymeric layer related to an ongoing electrolyte decomposition (44) and/or significant volume changes upon (de-)lithiation (98).

Transferring their knowledge about electronically conductive carbonaceous percolating networks (102) to conversion-alloying materials, Bresser *et al.* (94) very recently succeeded in overcoming these issues by coating ZnFe_2O_4 nanoparticles with an amorphous carbon layer. The use of rather stiff sodium-carboxymethyl cellulose (CMC; water-based) as binder

further enhanced the electrochemical performance, preventing the electrode morphology upon cycling (94), while the choice of the carbon precursor obviously also had a great impact on the cycling stability (103). After investigating the reaction kinetics of the involved electrochemical mechanisms of the carbon-coated ZnFe_2O_4 (94), very recently Varzi *et al.* (104) were able to realise a high-power LIB, comprising carbon-coated ZnFe_2O_4 nanoparticles as an anode and a composite of LiFePO_4 and multiwalled carbon nanotubes as cathode (Figure 5). This lithium-ion full-cell retained 85% of its initial capacity after 10,000 cycles at a current rate as high as 10 C with respect to the (capacity-limiting) cathode or about 3 C in regard to the ZnFe_2O_4 -C anode. To compensate the high first-cycle irreversible capacity Varzi *et al.* investigated different degrees of partial pre-lithiation of the anode. Remarkably, even the most extensive lithium doping (600 mAh g^{-1}) did not significantly affect the rate performance of the carbon-coated ZnFe_2O_4 nanoparticles, while at the same time the degree of pre-lithiation allowed the overall voltage of the lithium-ion full-cell to be tailored (104). These promising results confirm that the concept of using conversion or preferably conversion-alloying high capacity anodes – despite the manifold issues these materials are facing – is a valuable approach to future challenges for LIBs.

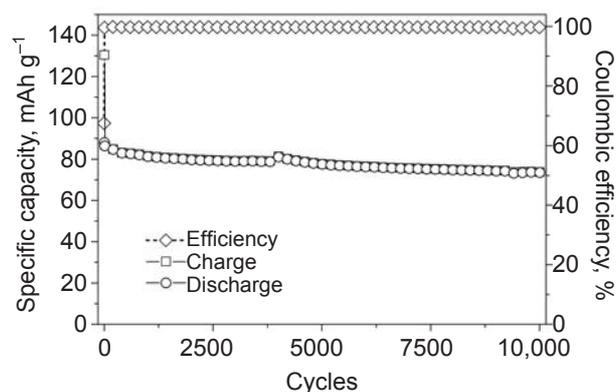


Fig. 5. Long-term cycling stability of a ZFO-C/LFP-CNT full-cell, applying a high current density (3 mA cm^{-2}) (Image courtesy of Alberto Varzi, Helmholtz Institute Ulm (HIU), Ulm, Germany)

5. Conclusions

This brief overview of commercial secondary LIB anodes reflects only partially the intensive and continuously growing research efforts carried out within the past 25 years in this specific segment of

LIB technology. It is also evident as the strict industrial requirements have so far allowed only a few materials to reach a commercial level, for which the guarantee of reliable performance is doubtlessly the most important requirement. As this article shows, even the change of basic reaction mechanisms from intercalation/insertion to alloying and conversion has not yet led to a breakthrough in LIB technology. We still do not have satisfactory solutions for the challenges within sight, but the encouraging advances and manifold developments of anode materials (and LIBs in general) from the first commercial device up to the present ones provide a solid basis for exploring the next generation of LIBs.

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