Insertion Electrode Materials for Rechargeable Lithium Batteries**

By Martin Winter, Jürgen O. Besenhard,* Michael E. Spahr, and Petr Novák

1. Introduction

1.1. Insertion Electrode Materials

Insertion electrode materials are included in the majority of ambient-temperature rechargeable batteries. The reason for their widespread application is the fact that electrochemical insertion ("electroinsertion") reactions are intrinsically simple and reversible. The term electroinsertion refers to a host/guest solid-state redox reaction involving electrochemical charge transfer coupled with insertion of mobile guest ions from an electrolyte into the structure of a solid host, which is a mixed electronic and ionic conductor. The major structural features of the host are kept after the insertion of the guests.[1]

To judge the benefits and problems of insertion electrodes in a rechargeable cell, some general properties of battery electrodes are discussed. Usually it is desirable that the amount of energy stored in a given mass or volume is as high as possible. To compare the energy content of cells, the terms "specific energy" (expressed in Wh/kg) and "energy density" (in Wh/L) are used, whereas the rate capability is expressed as "specific power" (in W/kg) and "power density" (in W/L).[20–23] To reach the goal of a high specific energy and energy density two fundamental requirements must be met by electrode materials: i) a high specific charge (in Ah/kg) and charge density (in Ah/L), i.e., a high number of available charge carriers per mass and volume unit of the material; and ii) a high (positive electrode) and low (negative electrode) standard redox potential of the respective electrode redox reaction, leading to a high cell voltage. Moreover, in rechargeable cells reac-

tions at both negative and positive electrode have to be highly reversible to maintain the specific charge for hundreds of charge/discharge cycles. This precondition is a fastidious demand. For comparison, in preparative chemistry a product yield of $\geq 90\%$ is usually considered to be sufficient, whereas a 90 % cycling efficiency of an electrode material (i.e., $\geq 90\%$ of the charge can be recovered in a charge/discharge cycle) is detrimental for application in rechargeable batteries. With an assumed cycling efficiency of even 99 % in each cycle the available specific charge after 100 cycles would be only ~37 % of the initial value (after 500 cycles less than 1 %). Thus, electrode materials should combine high specific charge with good rechargeability.

Reactions of insertion electrode materials are usually highly reversible. However, the mass and volume of the host material lower the specific charge. Moreover, the relatively slow transport of guests in the solid host limits the rate capability of the charge/discharge reaction. But wherever the reversibility of an electrode reaction is essential, the use of insertion electrode materials is favored. For example, the cell reactions of rechargeable aqueous batteries such as metal hydride/NiOOH or Zn/MnO_2 involve the reversible electroinsertion of H^+ into metal hydride[24–27] or MnO_2.[27–31] Even the reduction mechanism of PbO_2[32–34] (the positive electrode of the lead–acid accumulator) and $NiOOH$[35–40] (the positive electrode of the metal hydride/ NiOOH and Cd/NiOOH cells) are proposed to be associated with proton insertion.

Apart from protons no cations other than the small Li^+ can penetrate so easily into solids by insertion reactions. The idea of a rechargeable lithium cell based on Li^+ insertion reactions has been studied since the early 1970s, and numerous lithium insertion electrodes have been proposed to date. The principal concepts will be discussed on the basis of Figures 1a–d.

Since metallic lithium combines a very negative redox potential with a low equivalent weight, it is highly attractive for negative electrodes of high energy density batteries. Combined with a positive electrode material, such as a transition-metal oxide or chalcogenide, capable of reversible lithium insertion (e.g., MnO_2, MoS_2, or TiS_2) a rechargeable cell can be constructed (Fig. 1a). In the mid 1970s, rechargeable lithium systems using this concept were introduced to the market.[41–48] The positive electrode usually exhibits sufficient cycleability due to the reversible

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insertion mechanism but the periodic dissolution and deposition of metallic lithium during the cycling of the negative electrode is a serious problem. The cycling of metallic lithium is associated with extensive shape changes, and also side reactions with the electrolyte (corrosion of Li) occur. The latter cause considerable safety problems and reduce the cycle life of metallic lithium electrodes significantly.

In the 1980s there was a lot of enthusiasm about flexible lithium/polymer cells that use electroactive polymers such as polyaniline or polypyrrole as positive electrode materials (Fig. 1b; for a recent comprehensive review on electroactive polymers for rechargeable batteries see the literature[49]). The charging/discharging process of most of the conducting polymers is associated with the insertion/release of anions (X^-). Therefore, the salt concentration in the electrolyte changes during cycling because during discharge salt is formed from the cations of the negative electrode and anions of the positive electrode. Enough solvent must be provided to leave the salt LiX dissolved. This is unfavorable for the specific energy and operation of the battery.[7,50,51]

Replacement of the metallic lithium by lithium insertion compounds[7,52–63] improves both cell cycle life and safety but at the expense of cell voltage, specific charge, and rate capability. If an anion-inserting polymer is used as a counterelectrode (as in Fig. 1b), excess electrolyte is unavoid-

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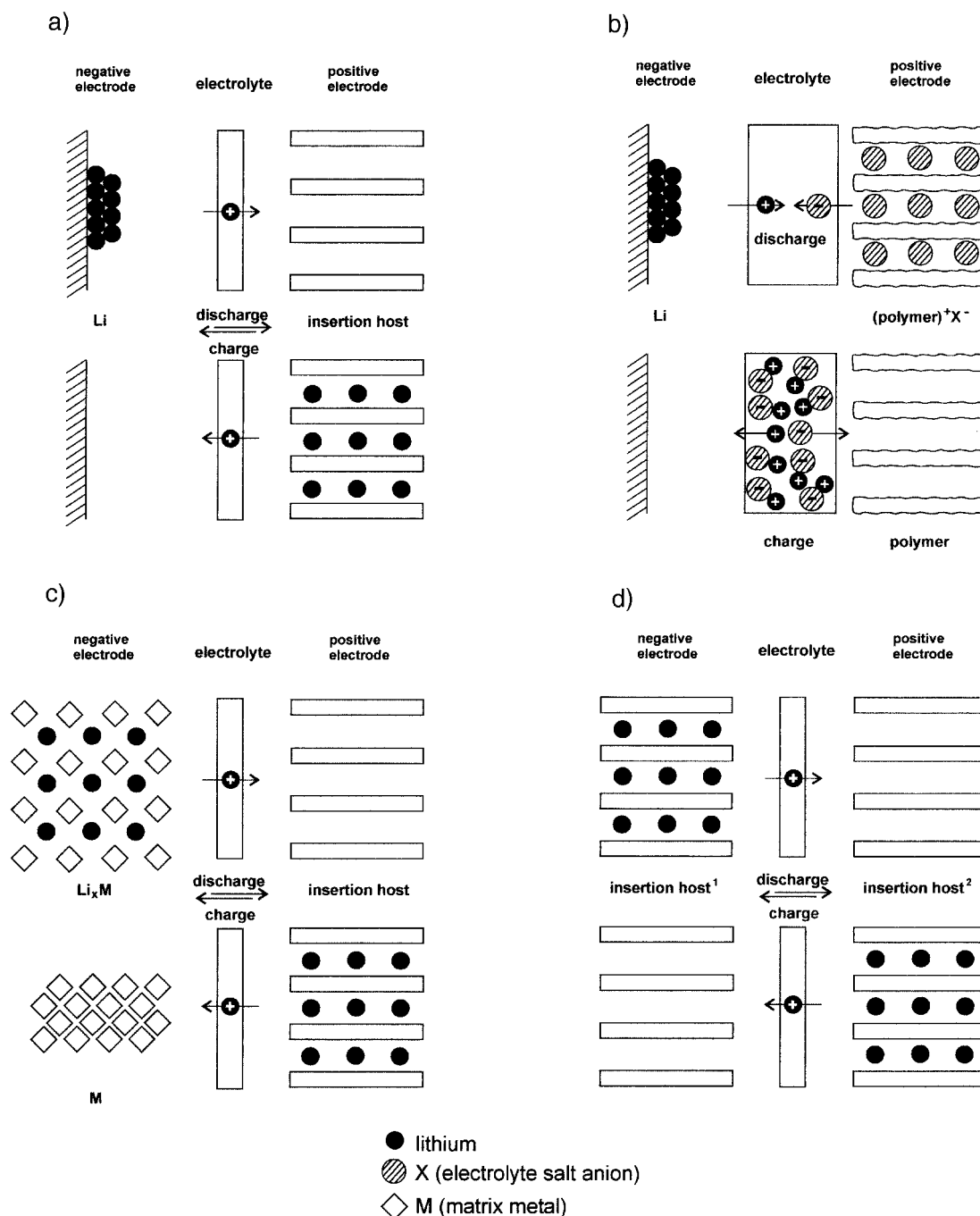
Fig. 1. Principal concepts of insertion electrode–based rechargeable lithium batteries (charged cell on the top, discharged cell below). a) Negative electrode: metallic Li; positive electrode: insertion host. b) Negative electrode: metallic Li; positive electrode: anion-exchanging electroactive polymer. c) Negative electrode: dimensionally unstable insertion host (Li alloy, Li_xM); positive electrode: dimensionally stable insertion host. d) Negative electrode: dimensionally stable insertion host; positive electrode: dimensionally stable insertion host.

able.[64–67] In contrast, a combination of a negative Li+ insertion electrode material with another Li+ insertion material having a more positive redox potential gives a Li+ ion transfer cell. One of the electrode materials deinserts (releases) Li+, which is inserted into the other (Figs. 1c,d). The basic electrochemistry involves only the transfer of Li+ cations between the two insertion electrodes, so that the electrolyte volume can be minimized to a very thin film. The

ion transfer principle was first proposed by Armand[15] and Scrosati and co-workers,[68,69] who named them "rocking chair" batteries.[59,60,68–73] Other names are "SWING",[74–76] "shuttlecock",[77,78] "Li-ion", or "Lion" cells".[79–84]

The cycleability of Li+ ion transfer cells depends mainly on the dimensional stability of the host material during insertion and deinsertion of Li+. For Li alloy–based electrodes the volume difference between the Li alloy and the

corresponding lithium-free matrix metal is typically of the order of ~100 % (Fig. 1c). Mechanical stresses occur during charge/discharge cycles, causing cracks. Finally, the alloy becomes crumbly. Thus, the cycle life is very limited. In contrast, cells with two-dimensionally rather stable ("low strain") Li$^+$ insertion materials (Fig. 1d) with volume changes ≤ ~10 %, for example, carbons (negative electrode) and transition-metal oxides (positive electrode), show good cycling behavior. At the present time research and development activities are mainly focused on such highly reversible insertion materials.

1.2. Electrode/Electrolyte Compatibility

The voltage of rechargeable lithium cells may be as high as ~5 V. Hence, a wide electrochemical stability window of the electrolyte is crucial for the shelf and cycle life of the cells. Aqueous as well as many non-aqueous electrolytes cannot be used because their thermodynamic and/or kinetic potential windows of electrochemical stability are not wide enough.[85] Only some aprotic electrolytes can be employed. However, compared with aqueous electrolytes, they are rather expensive, generally flammable, often toxic, and their ionic conductivities are typically about two orders of magnitude lower. Discussing ionic conductivity, it has to be considered that the transference number of Li$^+$ is typically only about 0.3 in non-aqueous electrolytes, meaning that only about 1/3 of the ionic charge is typically transported due to the movement of Li$^+$ ions.[90–95] This is because in an electrolyte solution the solvation of the small Li$^+$ cation is usually stronger that the solvation of the corresponding bigger anion X$^-$, for example PF$_6^-$, ClO$_4^-$, BF$_4^-$, or N(SO$_2$CF$_3$)$_2^-$.[90,96] The Stokes' radius of solvated anions is considerably lower and, thus, the anion mobility is higher than that of solvated Li$^+$ cations. This limits the power density of a lithium cell, the electrochemistry of which strongly depends on Li$^+$ transport in the electrolyte. A main concept to partly counterbalance the high internal resistance induced by the low electrolyte conductivity is to make the electrolyte film as thin as possible, so that the Li$^+$ transport pathways are short.

Suitable non-aqueous electrolytes for rechargeable lithium cells employing insertion electrodes can be roughly divided into three groups: i) liquid, ii) solid, and iii) polymer. i) Typical *liquid electrolytes* consist of a lithium salt Li$^+$X$^-$ dissolved in an aprotic organic solvent or a mixture of, for example, esters or ethers.[90,96] Liquid inorganic electrolytes, for example, SO$_2$ based,[97–101] have found special applications. Ambient-temperature molten salts can also be used.[102] ii) In true *solid electrolytes* only Li$^+$ ions are mobile. The transference number of Li$^+$ is ~1. Other (much less mobile) ions in a solid electrolyte are arranged in a crystalline or glassy matrix in which Li$^+$ moves through vacant and/or interstitial sites. This type of Li$^+$ transport occurs in inorganic solid electrolytes. At ambient temperature

the ionic conductivity of solid electrolytes is poor. Thus, only very thin electrolyte films can be used.[103–113] iii) Common examples of organic *polymer electrolytes* are ion conducting polymers formed by the solvation of a lithium salt Li$^+$X$^-$ with high molecular weight "dry" polymers such as poly(ethylene oxide) (PEO).[50,51,114–119] These polymer electrolytes are often classified as "solid" Li$^+$ conducting electrolytes, although in contrast to the true solid electrolytes the contribution of the counteranion to the ionic conductivity is considerable. The advantages of polymer electrolytes are their high mechanical stability and flexibility, which allows: i) simple fabrication of thin electrolyte films, for example, by casting or spin-coating; and ii) various electrode and/or cell designs, for example, fabrication of composite electrodes containing both electroactive material and polymer electrolyte. The major drawback of polymer/salt complexes is their rather poor ambient-temperature conductivity. On the contrary, sufficiently conductive polymer electrolytes can be obtained by trapping liquid solutions of organic electrolytes in polymer matrices such as polyacrylonitrile (PAN) or poly(vinylidene fluoride) (PVDF). These "wet" two-phase solid electrolytes combine the advantageous mechanical properties of the polymer with the chemical and electrochemical properties of liquid organic electrolytes.[114,117–127] In the following text we will discuss primarily the reactions of insertion materials in liquid organic electrolytes.

Lithium cells with non-aqueous electrolytes typically function far beyond the thermodynamical stability limits of the electrolyte. Thus, at positive electrodes electrolyte oxidation usually occurs.[128–136] Moreover, electrolyte reduction takes place in cells embodying negative electrodes having potentials close to that of metallic lithium (about –3 V vs. NHE). The strong reducing power of metallic lithium leads to its thermodynamic instability in most known battery electrolytes. Fortunately, in suitable electrolytes, films of electrolyte decomposition products spontaneously form after the immersion of Li into the electrolyte solution. The films protect the surface of the metal from further corrosion. Similar films were detected also on negative lithium insertion electrode materials, for example, on lithium-rich alloys and lithium/carbon intercalation compounds. These films have unique characteristics that favor the use of metallic Li over other metal electrodes with very negative redox potentials, such as Na, K, and Mg. The electronically insulating films (solid electrolyte interphase, SEI) on Li act as a "sieve" permeable only to the charge carrier Li$^+$ but impermeable to other electrolyte components.[137,138] In contrast, products of electrolyte decomposition at alkali metal electrodes other than Li are typically partially soluble and therefore do not form protective films.[139,140] Films formed on Mg are highly passivating.[137,139,141–147]

The composition and morphology of the SEI layers on metallic lithium depend on the kind of electrolyte used.[137,138,148–167] There is general agreement that films

formed in organic solvent–based electrolytes comprise: i) thick, porous, electrolyte permeable films of organic (polymeric and oligomeric) decomposition products; and ii) thin, compact, electrolyte impermeable films of inorganic decomposition products (Fig. 2). SEI films (compact and porous ones) were also observed in inorganic electrolytes.[168–175] The film formation on negative electrodes in organic electrolytes is generally irreversible but, in some inorganic electrolytes, films may be removed under certain charge/discharge conditions.[98–100] It should be stressed that whereas the presence of protective films on negative electrodes is widely accepted, films and/or interface effects on positive electrodes have been discussed only occasionally.[79,130,176–179]
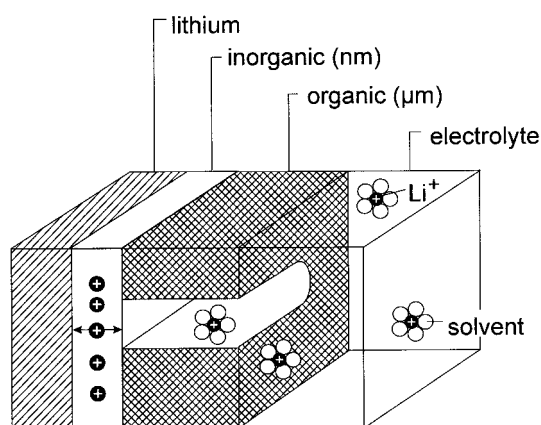

Fig. 2. Schematic drawing of films formed on metallic lithium in organic electrolytes (redrawn from [7]).

The observation of the kinetic stability of lithium in a number of non-aqueous electrolytes induced a rapid proliferation of research in the field of lithium batteries beginning in the 1950s, and the commercialization of primary lithium batteries followed quickly in the late 1960s and early 1970s.[20–23,52,180–196] Today, primary lithium cells have a variety of applications and commercial interest is still growing.[7,52,197–202]

However, apart from the rechargeable Li/MnO_2 cell commercialized by Tadiran (Israel),[203–205] the commercial breakthrough of rechargeable batteries based on metallic lithium failed. Upon recharge in liquid electrolytes lithium plating occurs simultaneously with some lithium corrosion and passivation (formation of SEI). Lithium typically deposits as dendritic,[206] highly reactive metal particles.[42,137,148,162,207–218] The dendrites are covered with SEI and therefore become partly electrochemically inactive, which reduces the cycle life of the cell. Moreover, the dendrites may form filaments that locally short-circuit the cell. Due to the low melting point of metallic Li (about 180 °C) the local overheat can trigger a disastrous thermal runaway.[216,219–221]

Several approaches have been pursued to improve the rechargeability and reliability of the metallic lithium electrode: i) by using liquid electrolytes that are less reactive toward lithium (e.g., highly purified or "additive-stabilized" electrolytes);[96,153,157,158,164,222–234] ii) by using polymer electrolytes;[49,50,114–118,163,217,235] iii) by adding surface active agents such as hydrocarbons, quarternary ammonium salts, and others that level the regrowth of metallic lithium;[208,209,215,227,228,236–239] iv) by controlling the properties of the metal surface and of the SEI using additives such as CO_2,[151,164,240–249] N_2O,[240] S_x^{2-},[240,250] HF,[162,251–255] and H_2O[164,243,256] (the additives may influence both the film formation and lithium plating process); v) by coating the lithium with a lithium-ion conducting membrane;[257–260] vi) by adding scavengers to the electrolyte that dissolve the dendritic lithium filaments;[148,180] vii) by using mechanical pressure to suppress dendritic lithium growth;[46,261,262] and viii) by "low-temperature pre-cycling".[263,264] However, all of the above attempts brought only partial improvements to the cycle life of the lithium electrode. The most successful approach to overcoming the problems with the metallic lithium electrode was the use of insertion electrode materials instead of Li metal.

2. Lithium Insertion Materials for Negative Electrodes

Various insertion materials have been proposed for negative electrodes of rechargeable lithium batteries, for example, transition-metal oxides and chalcogenides, carbons, lithium alloys, and polymers. Table 1 shows that both the

Table 1. Characteristics of representative negative electrode materials for lithium batteries, calculated by using data from [12,52,265–267]. The values are for fully lithiated host materials except for the values in parentheses, which are for lithium-free host materials. Li_4 denotes a four-fold lithium excess, which is necessary to reach a sufficient cycle life.

Negative electrode material	Molecular weight		Density [kg/L]		Theoretical specific charge [a] [Ah/kg]		Theoretical charge density [a] [Ah/L]	
Li (primary)	6.94		0.53		3862		2047	
Li_4 (secondary)	27.76		0.53		965		511	
LiC_6 (graphite)	79.00	(72.06)	2.24	(2.25)	339	(372)	759	(837)
LiAl	33.92	(26.98)	1.75	(2.70)	790	(993)	1383	(2681)
$Li_{21}Sn_5$	739.31	(593.55)	2.55	(7.28)	761	(948)	1941	(6901)
$LiWO_2$	222.79	(215.85)	11.30	(12.11)	120	(124)	1356	(1502)
$LiMoO_2$	134.88	(127.94)	6.06	(6.47)	199	(209)	1206	(1352)
$LiTiS_2$	118.94	(112.01)	3.06	(3.22)	225	(239)	689	(782)

[a] In some cases a considerably lower amount of the specific charge/charge density can be cycled reversibly in practice.

specific charges and the charge densities of lithium insertion materials are theoretically lower than that of metallic lithium. However, considering that the cycling efficiency of metallic lithium is ≤99 %, one has to employ a large excess of lithium[52,75,76,221] to reach sufficient cycle life. The practical charge density of a secondary lithium electrode is therefore much lower than the theoretical one, so that it is comparable with the charge densities of alternative lithium-containing compounds. However, the potential of the electrode materials also has to be considered because a higher potential versus Li/Li$^+$ of the negative electrode means a lower cell voltage. For instance, the potential of many Li alloys is ~0.3 to ~1.0 V vs. Li/Li$^+$ whereas it is only ~0.1 V vs. Li/Li$^+$ for graphite (Fig. 3).
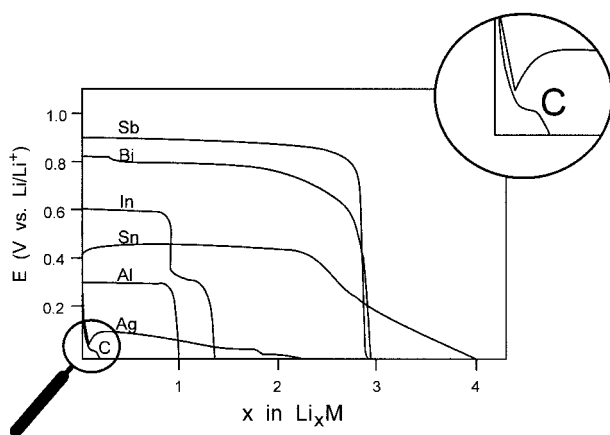

Fig. 3. Charging curves of some matrix metals (M), compared to highly oriented turbostratic mesophase pitch carbon fibers (P 100, FMI Composites-Union Carbide, characterized in LiClO$_4$ / propylene carbonate). Modified and redrawn from [268].

2.1. Oxides, Chalcogenides, Nitrides, and Organic Polymers as Negative Insertion Electrode Materials

Early Li$^+$ ion transfer systems used negative electrodes containing transition-metal oxides or chalcogenides with low redox potentials, for example, MoO$_2$,[12,269] WO$_2$,[12,68–71,270,271] or TiS$_2$.[12,56,272–276] These materials show rather low specific charges (Table 1) and, if combined with an oxidic positive electrode, rather low cell voltage. However, the low cell voltage (~1.5 V to ~2 V) makes these cells fairly safe (some of them can even use aqueous electrolytes).[86–89,277] "Low voltage" oxides, for example, TiO$_2$,[278–280] are still under development for special applications. Recent papers proposed novel oxidic negative electrode materials such as Li$_x$MVO$_4$ (M = Co, Cd, Ni, Zn, $1 < x \leq 8$)[281] or MnV$_2$O$_{6+\delta}$ ($0 < \delta \leq 1$),[282] or lithium/metal nitrides[283–286] with high specific charge. However, the practical merit of these new materials cannot be judged yet.

Lithium ion–inserting polymers such as polyacetylene, polythiophene, or poly(*p*-phenylene) were also suggested as negative electrodes but they have moderate specific charges and a rather poor stability.[49–51,56,287]

2.2. Lithium Alloys as Negative Insertion Electrode Materials

The replacement of metallic lithium by lithium alloys has been under investigation since Dey[288] demonstrated the feasibility of electrochemical formation of lithium alloys in liquid organic electrolytes in 1971. The reaction usually proceeds reversibly according to the general scheme shown in Equation 1.

$$Li_x M \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} x\,Li^+ + x\,e^- + M \qquad (1)$$
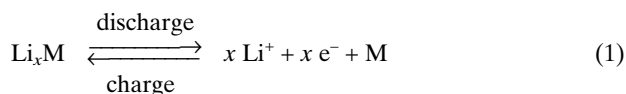
With only a few exceptions (such as hard metals, M = Ti, Ni, Mo, Nb), Li alloys are formed at ambient temperature by polarizing the metal M sufficiently negatively in a Li$^+$-containing electrolyte. In most cases even the binary systems Li–M are very complex. Sequences of stoichiometric intermetallic compounds and phases Li$_x$M with considerable phase range are usually formed during lithiation of the metal M, characterized by several steps and/or slopes in the charge diagram (Fig. 3). The formation of Li–M phases is in many cases reversible, so that subsequent steps and slopes can also be observed during discharge.

Among the matrix metals, M, that form Li alloys electrochemically, for example, Al, Si, Sn, Pb, In, Bi, Sb, Ag, and some multinary alloys,[7,56,61,63,265,289–308] aluminum alloys[271,288,309–326] have been studied most carefully. Generally, the matrix metals undergo major structural changes while alloying with lithium. Also, in the case of pure aluminum, alloying with lithium occurs with several successive phase formations: the formation of the α-phase (up to ~7 at.-% Li in LiAl), β-phase (a non-stoichiometric phase with ~47 to ~56 at.-% Li), and several lithium-rich phases.[309,318,322] The lithium alloy denoted in the technical literature as "LiAl" is frequently used as an insertion electrode material. It is a two-phase mixture of the α-phase and the β-phase. During discharge some Li remains in the Al (the α-phase is kept, only the β-phase is cycled), so that the Li$_x$Al is cycled within the stoichiometric range of ~0.1 $< x <$ ~1 (~50 at.-% Li).[318]

The matrix metal accepts negative charges during the insertion of Li$^+$ cations, forming a composite $(Li^+Al^-)_x Al^0$. The Al$^-$ ions formed by the charge-transfer reaction Al^0 + e$^- \Leftrightarrow$ Al$^-$ are considerably larger than neutral Al^0 atoms. Thus, the electrochemical cycling of LiAl (and also of other Li-alloy electrodes) is associated with large volume changes.[7,56,61,63,327–329] Lithium alloys Li$_x$M are of highly ionic character ("Zintl phases", Li$_x^{x+}$M^{x-}). For this reason they are usually fairly brittle. Thus, mechanical stresses, related to the volume changes, induce a rapid decay in mechanical properties and, finally, "pulverization" of the electrode.

The charge densities of Li alloys are high however. Moreover, the Li$^+$ mobility at room temperature in Li-rich

phases is quite acceptable and reasonable current densities can be achieved for charging and discharging.[289,291, 294,295,318,324,326,330–332] Therefore there have been many attempts to improve the dimensional stability of alloy electrodes during cycling. The metallurgical structure and morphology of Li alloys (grain size, shape, texture, and orientation) strongly affect their dimensional stability.[268,333–339] Thick electrodes consisting of large alloy particles are not flexible enough and degrade mechanically during cycling. A limitation of the cycling depth to very thin reaction layers[322,334,340–344] improves the cycleability. However, the specific charge with respect to the total electrode mass is low. This approach has been applied to alloy electrodes in rechargeable coin cells.[300,344–347]

One possibility for counteracting the mechanical degradation is the use of thin layers of alloys with small particle size materials ("submicro- or nanomaterials"). In such layers relatively large dimensional changes of the crystallites (~100 %) do not cause particle cracking, as the absolute changes in the particle dimensions are small. Thus, electrode pulverization is suppressed. For instance, micro- and submicrostructured multiphase matrix alloys show a large improvement in the cycling performance. In this case the more reactive particles can also expand in the first charging (alloying) step into ductile surroundings of still unreacted material.[268,337,338]

A similar concept of supporting small particles of electroactive Li alloys with less active or non-active matrices was introduced in 1981.[333] The matrix material can be a conductive polymer,[348,349] a porous membrane,[350] an inert metal-like copper,[327] or another mixed conductor.[289,291, 333,334] If the mixed conductor matrix material is another Li alloy $Li_xM^\#$, cycling has to be limited to a potential range in which Li^+ ions are not removed from $Li_xM^\#$.

Also carbons containing dispersed Li^+-alloying metals such as silicon[351,352] or silver[353–356] show good cycling behavior. Independent of the lithium alloying into the metal, lithium insertion into the carbon occurs in this case.

A Li^+ ion transfer cell with the trademark Stalion, announced recently by Fujifilm Celltech Co., Ltd.,[357] uses an "amorphous tin–based composite oxide (abbreviated TCO or ATCO)" for the negative electrode. The TCO combines both: i) a promising cycle life and ii) a high specific charge (>600 Ah/kg) and charge density (>2200 Ah/L).[358,359]

The TCO is synthesized from SnO, B_2O_3, $Sn_2P_2O_7$, Al_2O_3, and other precursors. However, only the Sn^{II} compounds in the composite oxide are said to form the electrochemically active centers for Li insertion. The oxides of B, P, or Al, which are electrochemically inactive, have glass-forming properties and form a network stabilizing the dimensional integrity of the composite host during synthesis.[359] The improvement of cycle life by using composite amorphous lithium insertion materials, such as V_2O_5, together with a network former, such as P_2O_5, has been reported in the literature.[270,360–365]

In order to explain the high specific charge a mechanism can be suggested in which the tin oxide reacts to form Li_2O and metallic Sn.[268,366–369] This reaction is associated with large charge losses due to the irreversible formation of Li_2O. In a second step the Sn then alloys with lithium reversibly. On the other hand, according to Fujifilm Celltech[359] no Li_2O was found after lithium insertion. However, the idea that the high specific charge of the TCO is due to the alloying of metallic tin has led to a renaissance of Li-alloy negative electrode research and development.[367–371]

2.3. Carbons as Negative Insertion Electrode Materials

At present mostly carbons are used as the negative electrode of commercial rechargeable lithium batteries: i) because they exhibit both higher specific charges and more negative redox potentials than most metal oxides, chalcogenides, and polymers; and ii) due to their dimensional stability, they show better cycling performance than Li alloys. The insertion of lithium into carbon, habitually named "intercalation", proceeds according to Equation 2.

$$Li_xC_n \xrightleftharpoons[\text{charge}]{\text{discharge}} x\,Li^+ + x\,e^- + C_n \qquad (2)$$
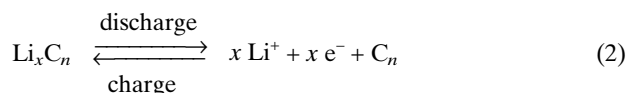
Due to electrochemical reduction (charge) of the carbon host, lithium ions from the electrolyte penetrate into the carbon and form a lithium/carbon intercalation compound, Li_xC_n. The reaction is reversible.

The quality of sites capable of lithium accommodation strongly depends on the crystallinity, the microstructure, and the micromorphology of the carbonaceous material.[7,56,77,221,287,290,372–386] Thus, the kind of carbon determines the current/potential characteristics of the electrochemical intercalation reaction, and also the risk of solvent co-intercalation. Carbonaceous materials suitable for lithium intercalation are commercially available in hundreds of types and qualities.[221,372,387–390] Many exotic carbons have been synthesized in laboratories by pyrolysis of various precursors, some of them with a remarkably high specific charge. Fullerenes have also been tested.[391–395]

Carbons that are capable of reversible lithium intercalation can roughly be classified as graphitic and non-graphitic (disordered). *Graphitic* carbons are carbonaceous materials with a layered structure but typically with a number of structural defects. From a crystallographic point of view the term "graphite" is only applicable to carbons having a layered lattice structure with a perfect stacking order of graphene layers, either the prevalent AB (hexagonal graphite, Fig. 4) or the less common ABC (rhombohedral graphite). Due to the small transformation energy of AB into ABC stacking (and vice versa), perfectly stacked graphite crystals are not readily available. Therefore, the term "graphite" is often used regardless of stacking order.
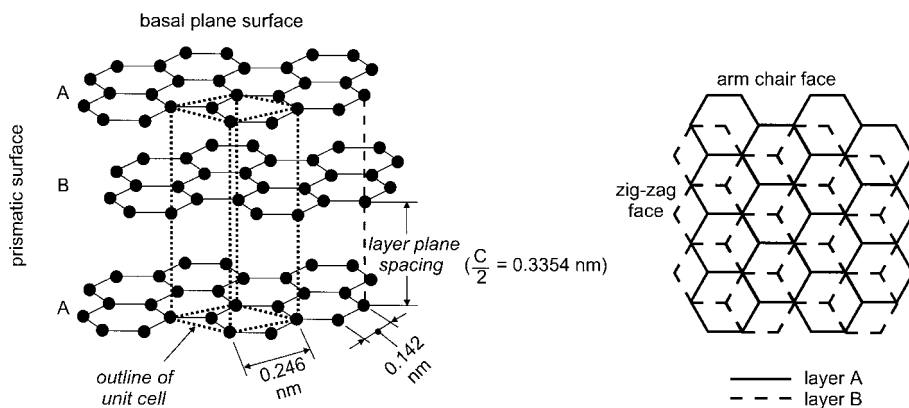
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Fig. 4. Left: schematic drawing of the crystal structure of hexagonal graphite, showing the AB layer stacking sequence and the unit cell. Right: view perpendicular to the basal plane of hexagonal graphite. Prismatic surfaces can be subdivided into arm-chair and zig-zag faces.

The actual structure of carbonaceous materials typically deviates more or less from the ideal graphite structure. Materials consisting of aggregates of graphite crystallites are named graphites as well. For instance, the terms natural graphite, artificial or synthetic graphite, and pyrolytic graphite are commonly used, although the materials are polycrystalline.[396] The crystallites may vary considerably in size. In some carbons, the aggregates are large and relatively free of defects, for example, in highly oriented pyrolytic graphite (HOPG). In addition to graphitic crystallites, other carbons also include crystallites containing carbon layers (or packages of stacked carbon layers) having significant misfits and misorientation angles of the stacked segments to each other (turbostratic orientation or turbostratic disorder).[397] The latter disorder can be identified from an increased average planar spacing compared to graphite.[396,398]

Non-graphitic carbonaceous materials consist of carbon atoms that are mainly arranged in a planar hexagonal network but without far-reaching crystallographic order in the *c*-direction. The structure of those carbons is characterized by amorphous areas embedding and crosslinking more graphitic ones[399–401] (Fig. 5). The number and the size of the areas vary, and depend on both the precursor material and the manufacturing temperature. Non-graphitic carbons are mostly prepared by pyrolysis of organic polymer or hydrocarbon precursors at temperatures below ~1500 °C. Heat treatment of most non-graphitic (disordered) carbons at temperatures from ~1500 to ~3000 °C allows one to distinguish between two different carbon types. Graphitizing carbons develop the graphite structure continuously during the heating process, as crosslinking between the carbon layers is weak and, therefore, the layers are mobile enough to form graphite-like crystallites. Non-graphitizing carbons show no true development of the graphite structure even at high temperatures (2500–3000 °C), since the carbon layers are immobilized by crosslinking. Since non-graphitizing carbons are mechanically harder than graphitizing ones, it is common to divide the non-graphitic carbons into "soft" and "hard" carbons.[399]

Because many carbon samples contain both graphitic and non-graphitic structural units, the classification into
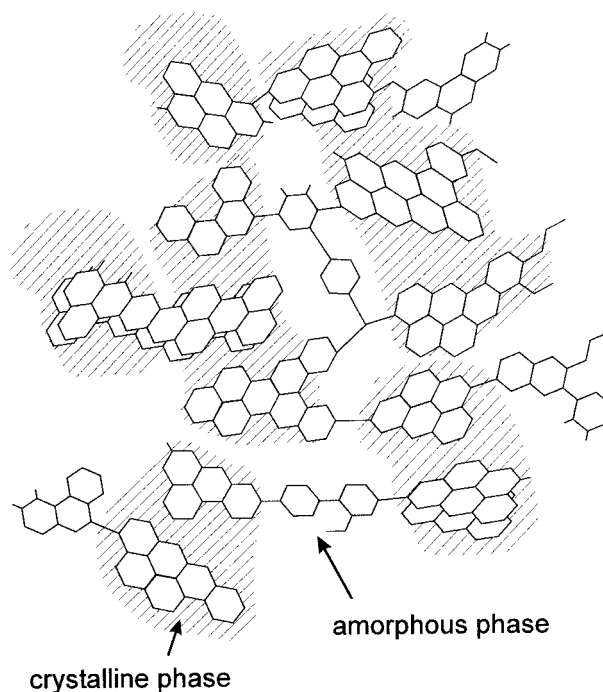

Fig. 5. Schematic drawing of a non-graphitic (disordered) carbonaceous material.

graphitic and non-graphitic types is sometimes arbitrary. For more details on pyrolysis, carbonization, and graphitization processes see the literature.[396,399,402,403]

2.3.1. Lithium Intercalation into Graphitic Carbon Materials

The synthesis of lithium–graphite intercalation compounds, Li_xC_n, (abbreviated as GIC) has been known since the mid 1950s.[404,405] At ambient pressure, a maximum lithium content of one Li guest atom per six carbon host atoms can be reached for highly crystalline graphitic carbons ($n \geq 6$ in LiC_n or $x \leq 1$ in Li_xC_6). The intercalation reaction occurs only at prismatic surfaces (arm-chair and zig-zag faces). Through the basal planes, intercalation is possible at defect sites only.[406] During intercalation into

graphite the stacking order of the carbon layers (named graphene layers) shifts to AA. Thus, two neighboring graphene layers in LiC_6 directly face each other (Fig. 6a). Owing to lithium intercalation the interlayer distance between the graphene layers increases moderately (10.3 % has been calculated for LiC_6).[267,407] The stacking order of the lithium interlayers is αα (a Li−C_6−Li−C_6−Li chain exists along the *c*-axis).[408,409] In LiC_6 the lithium is distributed in-plane in such a manner that it avoids the occupation of the nearest neighbor sites (Fig. 6b).
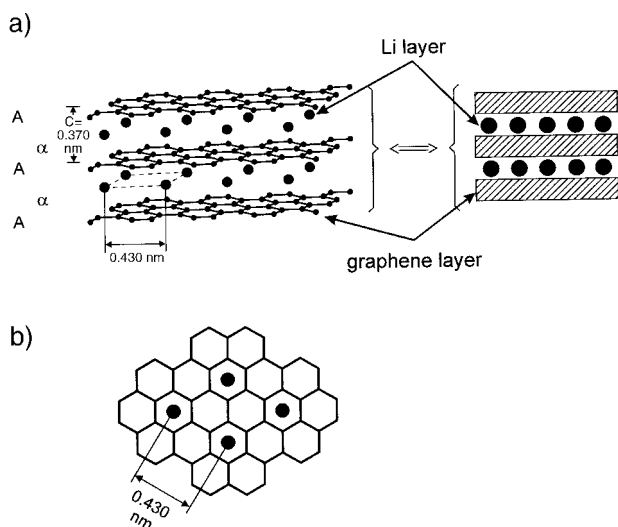
a)

b)

Fig. 6. Structure of LiC_6. a) Left: schematic drawing showing the AA layer stacking sequence and the αα interlayer ordering of the intercalated lithium. Right: simplified representation. b) View perpendicular to the basal plane of LiC_6.

A general feature of intercalation into graphite is the stepwise formation of a periodic array of unoccupied layer gaps at low concentrations of guest species, called stage formation.[17,404,405,410–415] This stepwise process can be described by the stage index, *s*, which is equal to the number of graphene layers between two nearest guest layers. Staging is a thermodynamic phenomenon related to: i) the energy required to expand the van der Waals gap between two graphene layers[63,415] and ii) the repulsive interactions between guest species. Thus, as a rule, few but highly occupied van der Waals gaps are energetically favored over a more random distribution of guests.

Staging phenomena can be easily observed during the electrochemical reduction of carbons in Li^+-containing electrolytes. Figure 7 (left) shows a schematic potential/composition curve for galvanostatic (constant current) reduction of graphite to LiC_6. The plateaus indicate two-phase regions (coexistence of two phases).[416,417] Under potentiodynamic control (linear potential sweep voltammetry, Fig. 7, right) the current peaks indicate the two-phase regions. Apart from the stage *s* = I, four[418] other binary phases, corresponding to the stages *s* = IV, III, II L, and II (which can also be obtained by chemical synthesis),[404,405,411,412,416,421–423] were identified from electrochemical curves and confirmed by X-ray diffraction[267,416,417,422–425] and Raman spectroscopy.[426] The splitting of the second stage into two, *s* = II (*x* = 0.5 in Li_xC_6) and *s* = II L (*x* = 0.33 in Li_xC_6), is due to different lithium packing densities.

Experimental galvanostatic curves for Li^+ intercalation into graphite clearly show the staging phenomenon (Fig. 8). Note that there are no sharp discontinuities be-
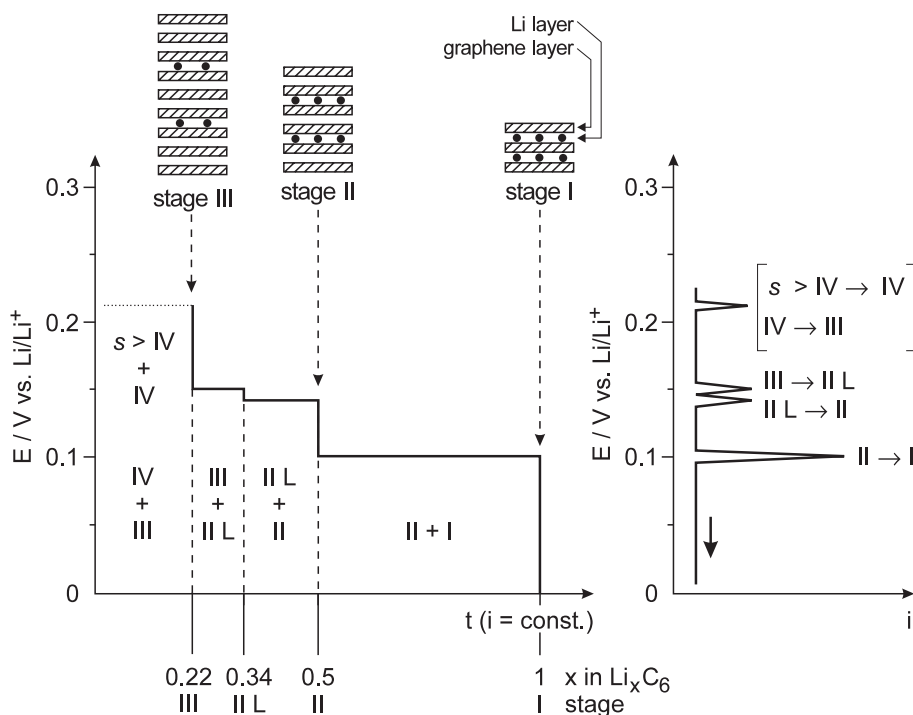

Fig. 7. Stage formation during electrochemical intercalation of lithium into graphite. Left: schematic galvanostatic curve. Right: schematic voltammetric curve. Modified and redrawn from [17].

tween the two-phase regions because: i) the packing density of Li_xC_6 varies slightly (a phase width exists) and ii) various types of overpotential cause plateau sloping in galvanostatic measurements (and peak broadening in voltammetric measurements). Theoretically, Li^+ intercalation into carbons is fully reversible. In practice, however, the charge consumed in the first cycle significantly exceeds the theoretical specific charge for the first stage LiC_6 of 372 Ah/kg (with respect to the mass of carbon, Fig. 8). The subsequent deintercalation of Li^+ recovers only about 80–95 % of this charge. In the second and subsequent cycles, however, charge consumption for Li^+ intercalation is lower and charge recovery is close to 100 %.
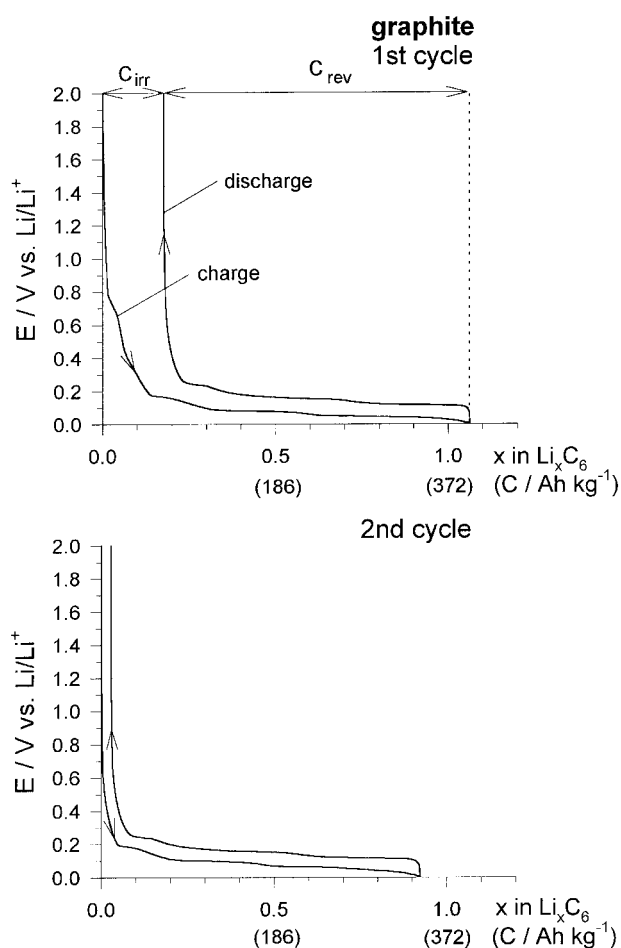

Fig. 8. Constant current charge/discharge curves (1st and 2nd cycle) of the graphite Timrex KS 44 in the electrolyte $LiN(SO_2CF_3)_2$/ethylene carbonate/dimethyl carbonate (C_{irr} is the irreversible specific charge, C_{rev} the reversible specific charge).

Commercial graphites can contain a considerable number of rhombohedral structural units. It has been reported that lithium intercalation mechanisms and storage capabilities are similar for both rhombohedral and hexagonal graphite structures.[388,390] However, the use of a graphite with a higher portion of rhombohedrally structured graph-

ene planes as lithium intercalation host is claimed to be advantageous in a recent patent.[427]

The excess charge consumed in the first cycle is generally ascribed to SEI formation and corrosion-like reactions of Li_xC_6.[221,428–432] Like metallic lithium and lithium-rich Li alloys, lithium/carbon intercalation compounds are thermodynamically unstable in all known electrolytes, and therefore the surfaces, which are exposed to the electrolyte, have to be kinetically protected by SEI films.[419,433–437] In contrast to the spontaneous film formation on metallic Li upon contact with electrolyte, the film formation on Li_xC_6 surfaces takes place as a charge-consuming side reaction in the first few Li^+ intercalation/deintercalation cycles, especially during the first reduction of the carbon host material. Even after film formation, the self-discharge rate of Li_xC_6 electrodes is considerable due to the reactivity of Li_xC_6 with the organic electrolyte. Some authors account additional effects to the poor charge recovery in the first cycle.[60,420,438–447]

Because of the irreversible consumption of material (lithium and electrolyte), the corresponding charge loss is frequently called "irreversible specific charge". The reversible lithium intercalation is called "reversible specific charge". Since the positive electrode is the lithium source in an ion transfer cell, charge and lithium losses are detrimental to the specific energy of the whole cell and have to be minimized for an optimum cell performance.

2.3.2. Effects of Electrolyte Composition

The irreversible specific charge is strongly affected by: i) the crystallinity and the morphology of the parent carbonaceous material and ii) the composition of the electrolyte (especially by the tendency towards solvent co-intercalation into highly graphitic matrices).[448] In 1970, Dey and Sullivan[449] reported the electrochemical decomposition of propylene carbonate (PC) on graphite electrodes at potentials of about 0.8 V positive to lithium deposition. In 1974 it was found that this reaction is accompanied by a partly reversible electrochemical intercalation of solvated lithium ions, $Li^+(solv)_y$, into the carbon host.[450] Since then, it is generally accepted that the intercalation of Li^+ and other alkali metal ions from organic donor solvent electrolytes into fairly crystalline graphitic carbons quite often leads to solvated (ternary) graphite intercalation compounds, $Li(solv)_yC_n$ (Fig. 9).[7,61,63,428,451–457] The so-called "solvated intercalation" is associated with extreme expansion of the graphite matrix (typically ~150 %), frequently leading to deterioration (exfoliation) of the graphite and as a result to a drastically decreased charge storage capability. The solvated intercalation compounds are thermodynamically favored over the corresponding binary compounds, that is, the potentials of their electrochemical formation are more positive than those for the formation of the corresponding binary GICs. This is true as long as the content of lithium
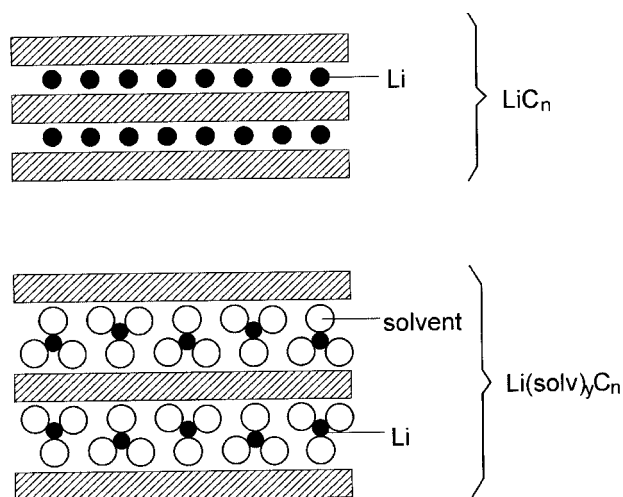
electrolytes, solvated lithium/graphite compounds also participate in the reactions. Film formation in the first cycle due to electrolyte decomposition at potentials of ~0.8 V vs. Li/Li$^+$ during the first reduction of the host material is not just a simple surface reaction but a rather complex three-dimensional process. Generally, reactions that cause irreversible charge losses in the first cycle can also take place on internal surfaces between the graphene layers via reduction of solvated lithium/graphite intercalation compounds. This reaction forms an "extra" film, which penetrates into the bulk of the graphite host (Fig. 10).[97,428,448,485,486] Several results indicate that the film formation process on graphite is even more complex.[419,437,485–487]

Fig. 9. Schematic drawing of binary (LiC$_n$) and ternary [Li(solv)$_y$C$_n$] lithium–graphite intercalation compounds. Modified and redrawn from [63].

in carbon is low ($x \leq 0.33$ in Li$_x$C$_6$). At this stage of Li$^+$ intercalation the coulombic interaction between the lithium guest layer (Li$^+$) and the balancing negative charge distributed over the graphene layers (C$_n^-$) is weak, and space to accommodate large solvent molecules is still available.[61,63,458,459]

The solvated GICs are thermodynamically unstable with respect to the reduction of the co-intercalated solvent molecules. This kinetically controlled reduction contributes considerably to the self-discharge of Li$_x$C$_6$ electrodes.[438,448,450,452,460–464] The solvated intercalation of lithium into carbon electrodes is therefore a serious problem. Particularly in the first few charge/discharge cycles, before the formation of the protective film on Li$_x$C$_6$ is finished, the tendency for solvent co-intercalation is high. Moreover, owing to the self discharge of Li$_x$C$_6$, the SEI film on the carbon electrode grows, thus increasing the internal resistance of the cell. Therefore, the power density of lithium ion cells with carbonaceous negative electrodes gradually decreases with the number of cycles.[79,240,465,466]

Since 1990[428] ethylene carbonate (EC) based electrolytes have been generally used to prevent the formation of Li$_x$-(solv)$_y$C$_6$. This is because the decomposition compounds of EC form an effective protective film on the external graphite surfaces in the early stages of the first reduction. The film prevents excessive solvent co-intercalation.[97,428,436,448] Since the viscosity of pure EC-based electrolytes is rather high, mixtures of EC with low viscosity solvents such as ethers (e.g., 1,2-dimethoxyethane (DME)[97,221,372,420,467] and 1,2-diethoxyethane (DEE)[468–471]) or more recently organic carbonates (e.g., dimethyl carbonate (DMC)[469–477] and diethyl carbonate (DEC)[433,434,471,475,476,478,479]) are preferred. A comparison of the performance of some electrolyte blends can be found in the literature.[475,476,480–484] Nevertheless, although the formation of binary lithium/graphite intercalation compounds prevails in EC-based
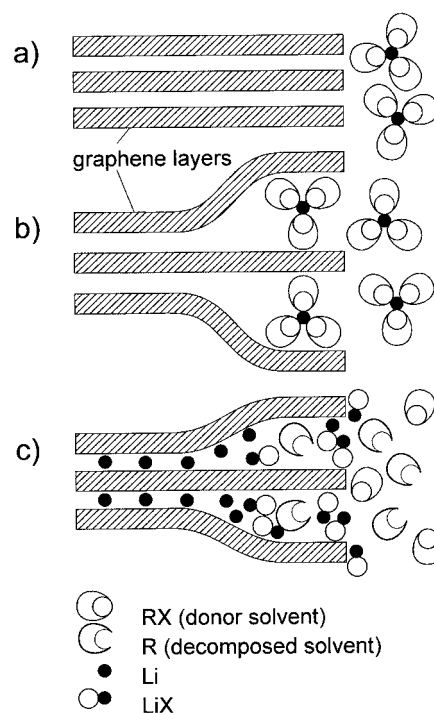

Fig. 10. Schematic model of the film-forming mechanism on/in graphite. a) Before reaction. b) Formation of ternary solvated lithium–graphite intercalation compounds Li$_x$(solv)$_y$C$_6$. c) Film formation due to decomposition of Li$_x$(solv)$_y$C$_6$. Modified and redrawn from [97].

Numerous research activities have focused on the improvement of the protective films and the suppression of solvent co-intercalation, either by proper choice of electrolyte components[467,488–499] or by pre-conditioning of the carbon electrode.[97,370,371,382,433,442–447,462,500–512] Significant improvements have been achieved by adding inorganic components to the base electrolyte, for example CO$_2$,[240,433,435,436,513–516] N$_2$O,[240] SO$_2$,[97,517–520] and S$_x^{2-}$.[240,250] The additives promote the formation of more compact and probably thinner inorganic films, which allow the selective penetration of unsolvated Li$^+$ cations. Films formed from organic decomposition compounds are supposed to be penetrated by organic solvent molecules rather easily.

2.3.3. Lithium Intercalation into Non-Graphitic Carbon Materials

From the point of view of electrochemical lithium intercalation, non-graphitic carbons can be classified with respect to their capability of reversible lithium storage. "High specific charge" carbons can store more lithium than graphite can ($x > 1$ in Li_xC_6). In contrast, carbonaceous materials that can incorporate only a considerably lower amount of lithium than graphite are called "low specific charge" carbons.

Graphitizing (soft) carbons such as turbostratic carbons[372,377,429,521–523] and more disordered carbons such as cokes[372,377,524–529] and carbon blacks[502,527,530] can be classified as "low specific charge" non-graphitic carbons because their maximum stoichiometric factor x in Li_xC_6 is typically ~0.5 to ~0.8 (for graphite, $x = 1$). In the case of turbostratic carbons, their rather low specific charge is partly due to the lower number of lithium sites available in "wrinkled" and "buckled" structural segments.[7,61] In addition, crosslinking of carbon sheets in disordered carbons hampers the shift to AA stacking, which is necessary for the accommodation of a higher lithium amount into graphitic sites.[521–523] Nevertheless, turbostratic carbons and cokes have found considerable interest as lithium host materials because crosslinking of the graphene layers mechanically suppresses the formation of $Li_x(solv)_yC_6$.[63,97,221,428] The use of composite carbonaceous materials comprising a "core" of graphite and a protective "shell" of disordered carbon combines the favorable lithium storage properties of graphite with the solvent co-intercalation retarding properties of non-graphitic carbons.[355,531–533] Figure 11 shows the first Li^+ intercalation/deintercalation cycle of a coke-containing electrode. The potential profile differs considerably from that of graphite, as the reversible intercalation of Li^+ begins at around 1.2 V vs. Li/Li^+, and the curve slopes without distinguishable plateaus. This behavior is a consequence of the disordered structure providing electronically and geometrically nonequivalent sites, whereas for a particular intercalation stage in highly crystalline graphite the sites are equivalent.[221,63]

Presently, much effort concentrates on the development of "high specific charge" carbonaceous materials. The carbons are synthesized at rather low temperatures from ~500 °C to ~1000 °C and show reversible specific charges from ~400 Ah/kg to ~2000 Ah/kg ($x = $ ~1.2 to ~5 in Li_xC_6), depending on the heat treatment temperature, organic precursor, and electrolyte used. Such materials have been known since the late 1980s, when several Japanese groups synthesized non-graphitic carbons with specific charges of ~300 Ah/kg to ~500 Ah/kg.[534–536] However, if lithium is stored in the carbon bulk, one can suppose that a higher specific charge requires a larger volume of the carbonaceous matrix to accommodate the lithium. This means that, although the specific charge (in Ah/kg) is higher than that of graphite, the charge density (in Ah/L) of both should be comparable.
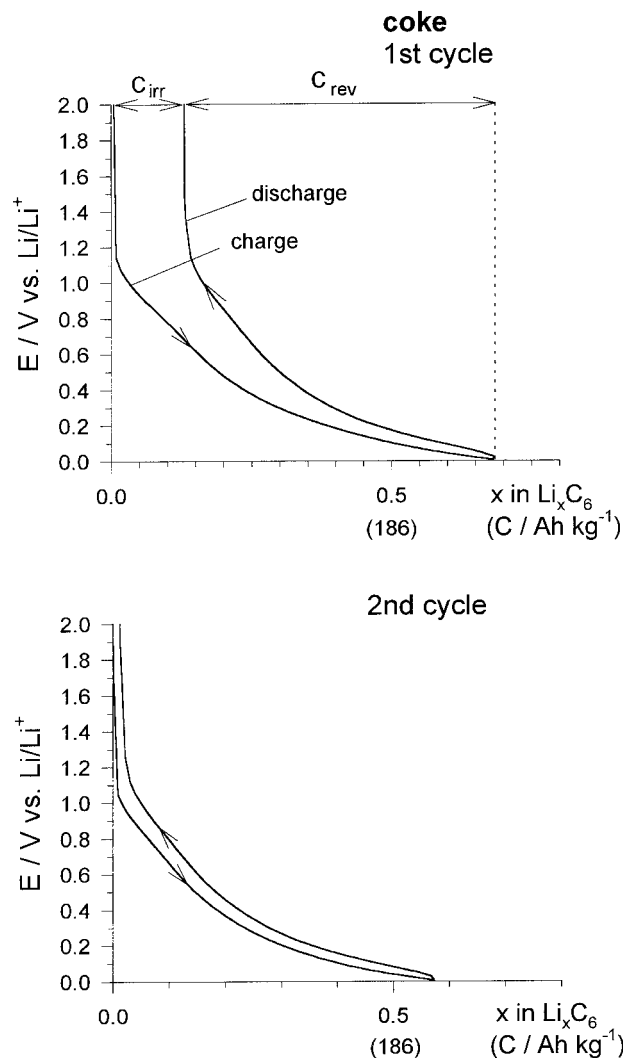

Fig. 11. Constant current charge/discharge curves (1st and 2nd cycle) of a coke (Conoco) in the electrolyte $LiN(SO_2CF_3)_2$/ethylene carbonate/dimethyl carbonate (C_{irr} is the irreversible specific charge, C_{rev} the reversible specific charge).

To explain the high specific charge, several (still rather controversial) models have been suggested. As discussed in the literature[380,381,537–539] some of the models are more probable than others. A few examples follow: Yazami et al.[290,540–544] proposed the formation of lithium multilayers on graphene sheets. Peled and co-workers[504,505] suggested that the extra charge reached by mild oxidation of graphite is attributable to the accommodation of lithium at the zigzag and arm-chair faces (Fig. 4) between two adjacent crystallites, and in the vicinity of defects and impurities. Sato et al.[545,546] suggested that lithium molecules occupy nearest neighbor sites in intercalated carbons (Fig. 12a). Others[287,503,547–549] proposed that additional lithium can be accommodated in nanoscopic cavities (Fig. 12b). Yata et al.[550] discussed the possibility of the formation of LiC_2 in carbons with high interlayer spacings of ~400 pm (graphite: 335 pm) for their "polyacenic semiconductor".[550–553] In

A ○ intercalated Li
B●─●B covalent Li$_2$ molecule

intercalated Li   Li in cavity

Li located between graphene layers

Li located at the surface of graphite particles

Li located at the edges of graphene layers

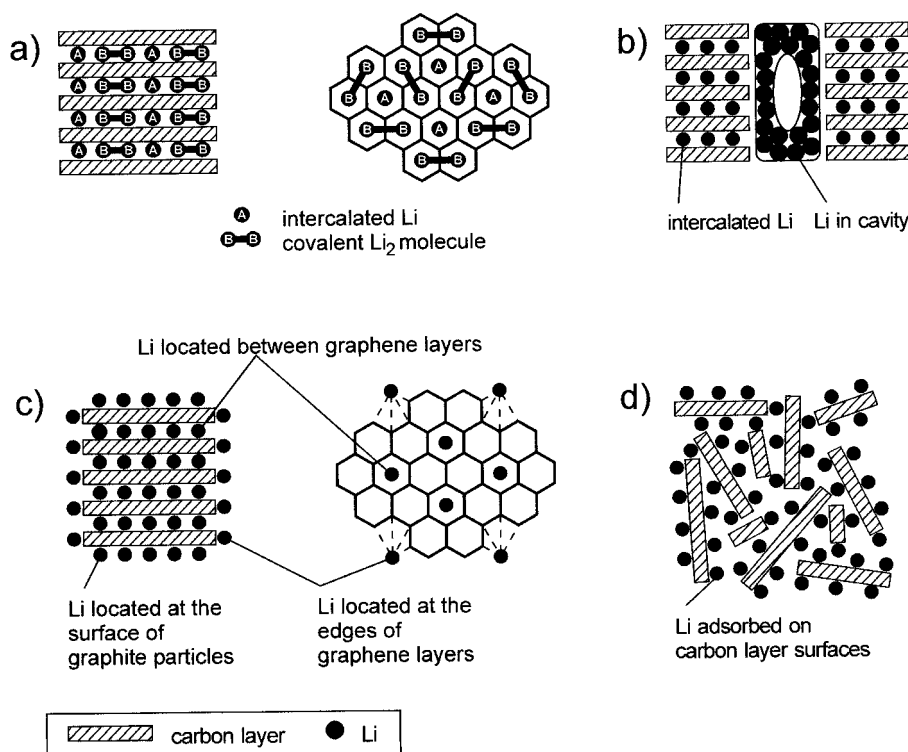Li adsorbed on carbon layer surfaces

▨▨▨ carbon layer   ● Li

Fig. 12. Schematic drawing of some mechanisms for reversible lithium storage in high specific charge carbonaceous materials as proposed in: a) [545], b) [287], c) [554], and d) [563].

the literature[554–559] it is assumed that small particle size carbons can store a considerable amount of lithium on graphite edges and surfaces in addition to the lithium located between the graphene layers (Fig. 12c). The existence of different "Li sites" has also been discussed.[560–562]

Several research groups (e.g., Dahn's group)[380,381,563–566] analyzed the behavior of the high specific charge carbons in detail. Both graphitizing (soft) and non-graphitizing (hard) carbons prepared below approximately 800–900 °C show very high specific charges, and exhibit a hysteresis: lithium uptake occurs close to 0 V vs. Li/Li$^+$ whereas lithium deinsertion occurs at much more positive potentials (Fig. 13).[380,381,551,565,566] The extent of the hysteresis is proportional to the hydrogen content in the carbon. It has been suggested that lithium is somehow bound near the hydrogen (see also the work of Wang et al.[567] and Zhou et al.[568]). Hydrogen is removed with increasing temperature. The specific charges achieved after the removal of hydrogen depend then on the structure of the carbonaceous material, that is, whether it is a soft or a hard carbon.[377,381,503,547,566,569–574] At temperatures above ~1000 °C the graphitizing (soft) carbons develop a structure similar to "low specific charge" carbons,[380,575,576] and rather low specific charges are observed ($x < ~0.5$ in Li$_x$C$_6$). If the heat treatment proceeds at higher temperatures and the fraction of stacked layers with graphitic order increases, the specific charge also increases.[573,574] By contrast, non-graphitizing (hard) carbons obtained at temperatures of ~1000 °C show little hysteresis. However, their high specific charge of several hundred Ah/kg can be reached only at a very low potential of a few millivolts versus Li/Li$^+$. In order to explain

high specific charge carbon
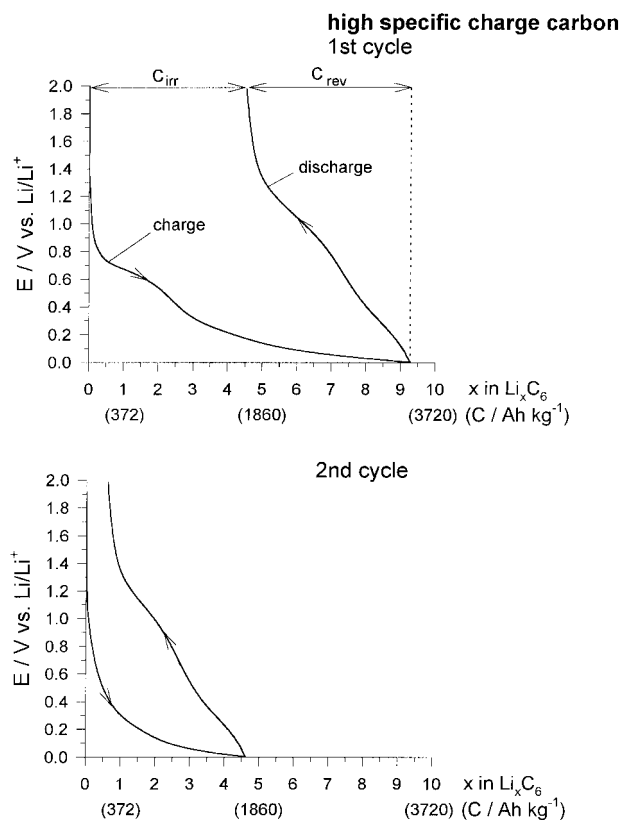**1st cycle**

2nd cycle

Fig. 13. Constant current charge/discharge curves (1st and 2nd cycle) of a high specific charge carbonaceous material (poly(*p*-phenylene), heat treated at 700 °C) in the electrolyte LiPF$_6$/ethylene carbonate/dimethyl carbonate (C_{irr} is the irreversible specific charge, C_{rev} the reversible specific charge).

this behavior Dahn et al.[380,563,575,577–579] suggested that lithium is "adsorbed" on both sides of single-layer sheets that are arranged like a "house of cards" or like "falling cards" (Fig. 12d). The "falling cards" model is the advanced form of the "house of cards" model and also regards the storage of lithium in micropores. Both the pore size and the pore openings should be small to avoid the reaction of stored lithium with the electrolyte.[381,563] In addition to microporosity microtexture should also be regarded.[580] Much work has also been done on evaluating carbons from inexpensive and abundant precursor materials.[564,578,579,581,582]

Heat treatment, considerably higher than 1000 °C, leads to a drastically reduced specific charge of hard carbons.[571,576] Although the high specific charge carbons show a multiple of the specific charge of graphite, they have some serious drawbacks: i) In many cases extremely high irreversible specific charges are observed,[374,380,381,503,550,552,560,563,583,584] occasionally also at higher cycle numbers.[381,560,583–585] ii) Carbons exhibiting hysteresis show poor cycling performance, and can be discharged only in a broad potential region of about 1–2 V (Fig. 13).[287,380,381,547–552,563,575,577,583] iii) Although the cycling performance of non-graphitizing (hard) carbons heat treated at ~1000 °C is good and almost no hysteresis occurs, the end of the charge potential of the carbons is very close to metallic lithium.[586] In some cases[381,563,575,577] the electrode was indeed charged to potentials negative of 0 V vs. Li/Li$^+$ to achieve the high specific charge. Under such a charging regime lithium deposition occurs. In contrast, there is a difference of approximately 0.1 V between the potential of graphitic LiC$_6$ and the potential of lithium deposition (Fig. 8). Therefore, there is a search for high specific charge carbons with graphite-like potential characteristics.[587,588]

Also the use of carbon insertion hosts containing one or more heteroatoms, such as boron,[221,372,589–593] silicon,[594–596] phosphorous,[597–602] or others,[221,603–607] leads in many cases to carbonaceous materials with increased specific charge for lithium insertion. The influence of the heteroatoms has been discussed on the basis of electronic[221,590,604] and steric effects.[597,598] However, the interaction of heteroatoms with the respective carbon neighbors has not been clarified entirely yet.[594,595] Moreover, data reported by different groups sometimes seems contradictory.[604,608] For more details see, for example, the reviews by Dahn et al.[221,372] and Riedel.[609]

3. Lithium Insertion Materials for Positive Electrodes

Numerous insertion/intercalation materials have been proposed for positive electrodes of rechargeable lithium batteries. These materials can be divided into three main groups: i) inorganic transition-metal oxides and chalcogenides, ii) organic molecules, and iii) polymers. However, the latter two groups have gained only subordinate importance for rechargeable battery systems so far despite the tremendous work that has been done especially on polymer film electrodes. A few books and review articles[49,610–615] as well as selected original papers[616–626], which will not be reviewed in this article, are recommended for insight into this work.

Graphite-based compounds were also suggested as positive electroactive materials. However, only the "graphite fluoride" (CF)$_n$ is of practical importance for primary lithium cells.[7,183,627] Li/(CF)$_n$ cells are not rechargeable because of the irreversible formation of the thermodynamically highly stable LiF at a discharge depth (lithium uptake) of about 50 % via an energetically favored displacement reaction.[628]

By far the largest number of positive electrode materials that are being discussed are inorganic transition-metal oxides or sulfides.[52] Table 2 supplies an overview of some of the materials that have been intensively evaluated. Their specific charges are based on a reversible range Δx of the lithium content during the charging/discharging process shown in Equation 3, where X = oxide or chalcogenide; $x \geq 0$.

$$\Delta x \, \text{Li}^+ + \Delta x \, \text{e}^- + \text{Li}_x\text{MX} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \text{Li}_{x+\Delta x}\text{MX} \qquad (3)$$
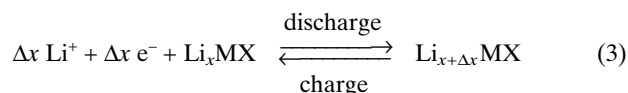
Table 2. Characteristics of representative positive electrode materials for lithium batteries [52]. The values are either for fully lithiated (discharged) host materials or lithium-free (charged) host materials, and the specific charges are based on a reversible range Δx of the lithium content during the charging/discharging process.

Positive electrode material	Molecular weight	Density [kg/L]	Reversible range Δx	Theoretical specific charge [Ah/kg]	Theoretical charge density [Ah/L]
Charged					
TiS$_2$	112.01	3.27	1	239	782
MoS$_2$	160.06	5.06	0.8	134	678
V$_2$O$_5$	181.88	3.36	1	147	495
V$_6$O$_{13}$	513.64	3.91	3.6	188	734
MnO$_2$	86.94	5.03	0.5	154	775
NbSe$_3$	329.81	8.7	3	244	2121
Discharged					
LiCoO$_2$	97.87	5.16	0.5	137	706
LiNiO$_2$	97.63	4.78	0.7	192	919
LiMn$_2$O$_4$	180.82	4.28	1	148	634

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Positive electrode materials that contain no lithium after their synthesis are in the charged state. They must be combined with negative electrodes that serve as a lithium source in the first discharge cycle. These non-lithiated positive electroactive materials usually electrochemically insert lithium at potentials negative of 3 V vs. Li/Li$^+$. In the lithiated state they are usually not stable to air and moisture. On the contrary, there are various lithium-containing materials that could serve as lithium source in electrochemical cells. They must be charged (the lithium must be deinserted) in a first formation cycle. These lithium-containing materials are typically stable to air and moisture, and electrochemically deinsert lithium in the 4 V potential region. According to their average insertion/deinsertion potentials it is common to classify the positive materials as "3 V" and "4 V" materials. However, in the following text we will take advantage of the structural classification of one-, two-, and three-dimensional transition-metal oxides and chalcogenides, based on the type of void spaces available for lithium insertion, as illustrated in Figure 14.

3.1. One-Dimensional Hosts

Transition-Metal Trichalcogenides: The electrochemically interesting representatives of this class of insertion hosts are crystalline TiS$_3$ and NbSe$_3$.[629–635] The crystal structures of TiS$_3$ and NbSe$_3$ are quite similar, consisting of chains of face-sharing trigonal prismatic [MX$_6$] units. The chains are staggered in such a way that the metal M can coordinate with two additional chalcogenides X from different adjacent chains to form a bicapped trigonal prism.[636,637] The resulting ribbons are linked together by weak van der Waals forces in the crystallographic *b*-direction, which leads to the fibrous morphology of the materials (Fig. 15). TiS$_3$ can be viewed as Ti^{4+}S$_2^{2-}$S^{2-} with a disulfide ion S$_2^{2-}$ and an isolated sulfide S^{2-}.[12] In NbSe$_3$ the negative charge is delocalized over the selenium atoms, localized Se–Se bonds are lacking.

Either electrochemically or chemically (using, e.g., butyllithium as a lithiation reagent), both compounds insert three lithium atoms per formula unit into their one-dimensional channels.[638–640] For TiS$_3$ the electrochemical insertion of the first two lithium leads to the reduction of the di-
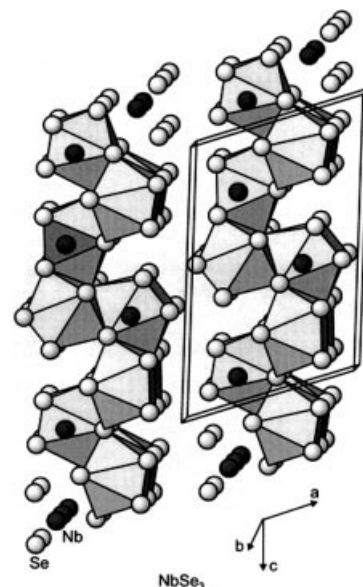

Fig. 15. The one-dimensional crystal structure of NbSe$_3$.

sulfide ions to isolated sulfide ions and is not reversible. This is owing to the rearrangement of TiS$_6$ groups from a trigonal prism to a more favored octahedron, thus forming one-dimensional chains for lithium incorporation. Although insertion of the third lithium is reversible, a large capacity fading is obtained in Li/TiS$_3$ cells during cycling.[641] In contrast to TiS$_3$, the electrochemical lithiation of NbSe$_3$ is quite reversible and of topochemical nature, since the trigonal prismatic coordination of niobium is more stable than octahedral coordination and no conversion is involved.[642] Both the lithium-free NbSe$_3$ and the lithiated compound Li$_3$NbSe$_3$ show metallic conductivity, which allows the fabrication of electrodes without the use of electronically conducting additives such as carbon black or graphite. The first discharge proceeds in two distinct steps: the flat plateau region at about 1.6 V vs. Li/Li$^+$ corresponds to the insertion of two lithium ions per one NbSe$_3$. The third Li$^+$ is inserted in a sloping region to 1.0 V. Subsequent cycling of the electrode evokes structural changes so that repeated discharges occur at higher potentials with a mid-discharge potential of about 1.8 V. Nevertheless, the toxicity, high cost, and rather low average discharge potential of 1.8 V have limited the long-term interest in NbSe$_3$.[635,643]
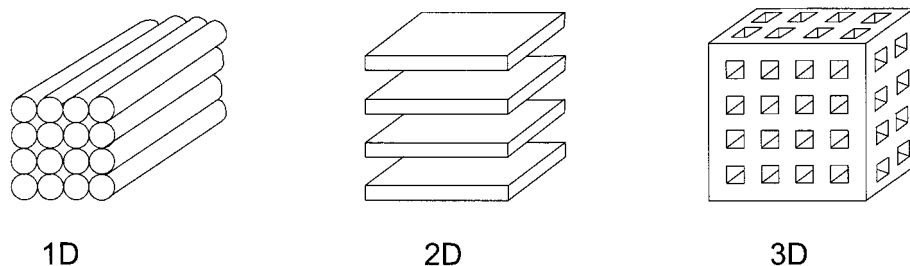

1D   2D   3D

Fig. 14. Schematic representation of void spaces in one-, two-, and three-dimensional transition-metal oxides and chalcogenides.

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3.2. Two-Dimensional Hosts

The most important two-dimensional insertion compound, graphite, was discussed in detail as a negative electrode material in the preceding chapter. Layered-type dichalcogenides of the transition metals Ti, Nb, Ta, Mo, and W, as well as dioxides of the transition metals V, Cr, Fe, Co, and Ni are of interest as positive insertion electrode materials[630,635,644–648] and will be discussed here.

3.2.1. Layered-Type Transition-Metal Dichalcogenides

The salient structural features of the transition-metal dichalcogenides MX_2 with a CdI_2-type structure are blocks of two hexagonally close-packed chalcogen layers between which the transition metals reside in either prismatic or octahedral coordination of six chalcogens. This coordination symmetry together with a different stacking arrangement of the X−M−X layers gives rise to the different polymorphs shown in Figure 16.[649]

The key feature of all these polymorphs is the van der Waals gap between the X−M−X sheets, which—as explained for graphite—provides the space for guest reactants in intercalation reactions. During the intercalation of lithium, a complete charge transfer occurs that involves the reduction of M^{4+} to M^{3+} and the diffusion of Li^+ into the van der Waals gaps,[650] resulting in the expansion of the host structure along the crystallographic c-direction. The van der Waals forces between the layers are thereby replaced by coulombic interactions. In all the polymorphs, octahedral and tetrahedral interstitial sites are available for the intercalation of lithium ions. In general, the octahedral sites are energetically more favored[651] leading to a maximum possible intercalation level of one lithium atom per formula unit. Diffusion of lithium proceeds via the tetrahedral sites. Particularly TiS_2 and NbS_2 tend to form metal-rich compounds $M_{1+y}X_2$ with excess metal in the van der Waals gap. This excess metal has been shown to slow the rate of intercalation of the $M_{1+y}X_2$ electrode.[652]

Among the transition-metal dichalcogenides TiS_2 in particular satisfies the criteria for a proper rechargeable electrode material. A high free energy for the lithium intercalation reaction, a single homogeneous phase of intercalation with only 10 % lattice expansion in the entire intercalation range of up to $x = 1$ in Li_xTiS_2, a good electronic conductivity in both the non-intercalated and lithiated state, and a fast lithium diffusion with a diffusion coefficient of about 10^{-12} m^2/s at room temperature (leading to high rate capability)[12] are the characteristics of TiS_2. An average discharge voltage of 2.1 V and an almost 100 % TiS_2 utilization result in a specific energy of about 450 Wh/kg of a rechargeable cell with metallic lithium negative electrode. The rechargeability of TiS_2 has been demonstrated in over 400 cycles with only 20 % loss in the electrode utilization.[3,12] For comparison, crystalline MoS_2 is stable only at low discharge depths of about 10 %. Intercalation of lithium into MoS_2 is accompanied by a structural change from prismatic to octahedral molybdenum coordination.[12,653] Due to the low free energy of formation of the host sulfide itself, a higher degree of lithium intercalation leads to the formation of Li_2S and Mo metal. However, a better electrode behavior with a high degree of reversibility and a continuous discharge profile was observed for amorphous MoS_2.[654]

3.2.2. Layered-Type Transition-Metal Dioxides

The structure of the two-dimensional lithium transition-metal oxides is shown in Figure 17. The oxides with the general formula $LiMO_2$ with M = V,[655] Cr,[656] Fe,[657] Co,[658] and Ni[659–661] adapt the α-$NaFeO_2$-type structure, which can be regarded as a distorted rock salt superstructure. In a cubic close-packed oxygen array the lithium and transition-metal atoms are distributed in the octahedral interstitial sites in such a way that MO_2 layers are formed consisting of edge-sharing $[MO_6]$ octahedra. In between these layers lithium resides in octahedral $[LiO_6]$ coordination, leading to alternating (111) planes of the cubic rock-
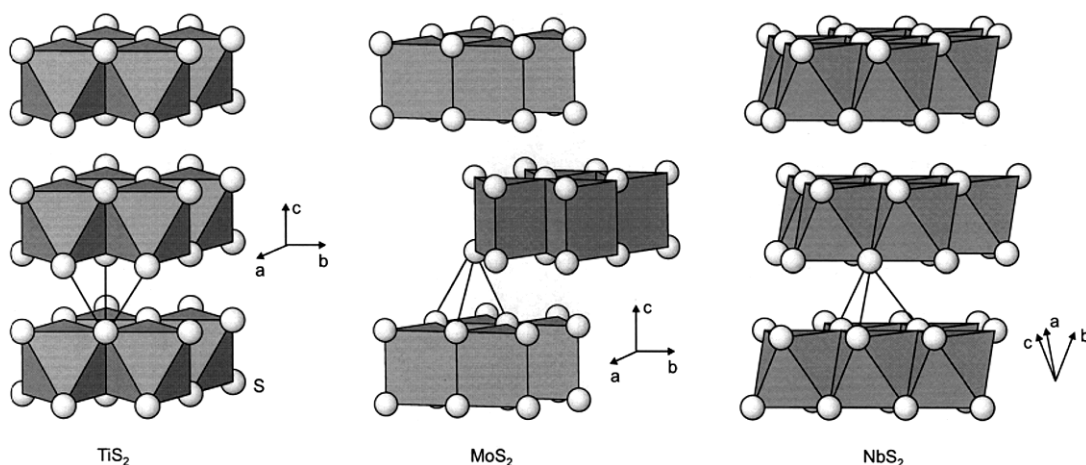

Fig. 16. The two-dimensional crystal structures of TiS_2, MoS_2, and NbS_2.
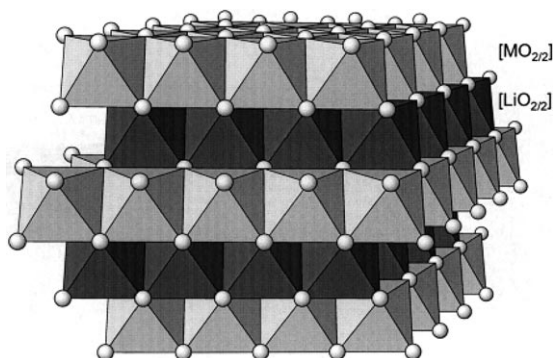
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Fig. 17. The two-dimensional crystal structure of LiMO$_2$ (M = Ni, Co, V, etc.) of the α-NaFeO$_2$ type.

salt structure (Fig. 17). This (111) ordering induces a slight distortion of the lattice to hexagonal symmetry. Complete deinsertion of the lithium ions results in the layered CdCl$_2$ structure type. The oxides are thermodynamically stable only in the intercalated state LiMO$_2$. The reason for this is the high electronegativity of oxygen, which leads to a higher ionic character of the metal–oxygen bonds in comparison to the covalent nature of metal–chalcogen bonds. The resulting negative charge of the transition metal–oxygen layers causes repulsive interactions between adjacent layers, which have to be compensated for by positively charged ions between the adjacent oxygen layers.[662–664] Among the above-mentioned isostructural dioxides, particularly LiCoO$_2$, LiNiO$_2$, and the mixed oxides Li(Co,Ni)O$_2$ have gained industrial importance as electrode materials.

LiCoO$_2$: The use of Li$_x$CoO$_2$ as lithiated positive electroactive material was suggested for the first time in 1980.[665,666] The Li/Li$_x$CoO$_2$ cells exhibit very high voltages with open circuit voltage (OCV) in the range from 3.9 to 4.7 V for stoichiometries of $0.07 < x < 1$. Thus, a very high specific energy of ca. 1070 Wh/kg is expected, based on an average discharge voltage of 3.9 V.

The course of the OCV vs. x curve is monotonous, which could mean that the intercalation process is influenced by a non-stoichiometry in the lithium sublattice of Li$_x$CoO$_2$. However, both high-precision voltage measurements and in situ X-ray diffraction measurements of Li$_x$CoO$_2$ indicate a sequence of three distinct phase transitions as x decreases from 1 to 0.4.[667,668] The first transition was shown to be of the first order, leading to co-existing phases for $0.75 < x < 0.93$, the other two transitions occur slightly above and below $x = 0.5$ and are order/disorder transitions of the lithium ions. The phase transition to the lithium-ordered phase is accompanied by a distortion from hexagonal to monoclinic symmetry. For LiCoO$_2$ prepared at high temperatures (800–900 °C) the first-order transition involves an increase in the c-lattice parameter of the hexagonal unit cell and an enlargement of the intersheet distance from ~4.7 Å to ~4.8 Å (~2 %) as well as a significant decrease in the Co–Co distances.[665,666,669] The increase in the interlayer distance can be explained by the increasing electrostatic repulsion of adjacent oxygen layers. The decrease in the Co–Co distances leads to a dispersion of the electronic energy bands assigned to the electron wavefunctions of the Co atoms.[670–672] This dispersion results in an overlap of the valence and conduction bands and explains the observed change from semiconducting to metallic conductivity during this phase transition.

Measurements of the lithium diffusion coefficient in LiCoO$_2$ gave values ranging approximately from 10^{-11} m^2/s to 10^{-12} m^2/s at room temperature, based on different techniques and interpretation approaches. These diffusion coefficients are slightly higher than those measured for TiS$_2$ and give evidence for a good lithium ion mobility.[129,671,673]

Although practically all the lithium in LiCoO$_2$ can be removed electrochemically, reversible cycling can be carried out only in a limited range of compositions. The reason is the highly oxidizing power of the almost delithiated Li$_x$CoO$_2$, which causes oxidative decomposition of the electrolyte under formation of polymeric films on the electrode surface,[671] and corrosion of the underlying current collector. Therefore, charging has to be restricted, for example, in the case of PC-based electrolytes, to $x > 0.35$.[129] Microcalorimetry on Li/LiCoO$_2$ cells with this electrolyte revealed reversible electrode reactions in the voltage range from 4.0 V to 1.2 V.[269] Above 4.0 V, however, heat is produced, indicating solvent oxidation.

The corrosion and solvent decomposition problems at high potentials triggered an intensive search for stable electrolytes, as well as for electrolytes or electrolyte additives that could form protective ion-permeable films on the electrode surface. Hambitzer's group presented Li/LiCoO$_2$ cells with a stable liquid inorganic electrolyte consisting of the liquid adduct LiAlCl$_4$·SO$_2$. The cells allow reversible cycling with high efficiency in the stoichiometry range $0.3 < x < 1.0$ at voltages of up to 4.5 V.[98,99,674–676] Overcharging of the cell to voltages of up to 5 V is possible without any degradation of the CoO$_2$ electrode. On overcharging, the AlCl$_4^-$ is oxidized, forming AlCl$_3$ and Cl$_2$. The high solubility of both reaction products in the electrolyte allows a recombination to the electrolyte salt at the lithium negative electrode according to Equation 4.

$$Cl_2 + 2\,AlCl_3 + 2\,Li \rightarrow 2\,LiAlCl_4 \qquad (4)$$

Various investigations have demonstrated a good cycleability of LiCoO$_2$ up to 4.3 V vs. Li/Li$^+$ in liquid organic,[82,245,269,677,678] polymeric,[273] and solid electrolytes.[679] The cycling stability favored the application of LiCoO$_2$ as positive electrode material in the first commercial rechargeable lithium ion transfer cells with carbon negative electrodes.[79]

The oxides synthesized at low temperatures have dissimilar structural and electrochemical properties to the above-discussed LiCoO$_2$ prepared at high temperatures (HT). Low-temperature LiCoO$_2$ (LT-LiCoO$_2$) can be prepared either at 400 °C using solid-state synthetic routes[680–686] or

via a solution technique.[687–690] LT-Li$_x$CoO$_2$ has a cubic close-packed oxygen lattice that remains unaffected by lithium extraction, in contrast to the trigonal high-temperature polymorph with a c/a ratio that increases from 4.99 at $x = 1$ to 5.12 at $x = 0.5$. The LT-Li$_x$CoO$_2$-containing electrodes discharge at potentials approximately 0.5 V more negative than HT-Li$_x$CoO$_2$, thus revealing weaker electrochemical oxidizing properties. However, the cycle life of the low-temperature polymorph is poor, which gives evidence for the intrinsic instability of the delithiated structure. High-resolution neutron diffraction indicated a cation distribution that is intermediate between an ideal layered structure and an ideal lithiated spinel structure.[684] This is supported by the fact that an acidic treatment of LT-LiCoO$_2$ leads to an almost ideal lithiated spinel compound Li$_2$[Co$_2$]O$_4$.[684] In contrast, detailed characterization of the samples prepared by the solution technique indicated a cubic disordered NaCl-type structure.[687] A lower Li$^+$ diffusion rate than for HT-LiCoO$_2$ as well as a high chemical reactivity in the charged state results in the formation of passivating surface films. This might be a further reason for the cycling instability of LT-LiCoO$_2$.[689] Acid-leached samples derived from Ni-doped LT-LiCo$_{1-y}$Ni$_y$O$_2$ compounds show a significantly improved cycling stability over LT-LiCoO$_2$.[691] The resulting spinel structure expands/contracts only by a factor of 0.2 % during the lithium insertion/extraction, which indicates the structural stability of the [Co$_2$]O$_4$ spinel framework towards the lithium insertion/extraction.

LiNiO$_2$: The isostructural LiNiO$_2$ is attracting intense attention not only because of its economic advantage over LiCoO$_2$ but also because the redox potential of LiNiO$_2$ (Fig. 18) is about 0.25 V more negative than that of LiCoO$_2$, making the former less prone to electrolyte oxidation problems.[692] Whereas with LiCoO$_2$ electrodes in liquid organic carbonate–based electrolytes only 0.46 Li$^+$/mol (125 Ah/kg of the oxide) can be attained in the potential range between 2.5 V and 4.3 V vs. Li/Li$^+$ (the expected stability window of the electrolyte), about 0.65 Li$^+$/mol

Fig. 18. The cyclic voltammogram of LiNiO$_2$.

(150 Ah/kg of the oxide) could be reached with LiNiO$_2$ electrodes between 2.5 V and 4.1 V during the first charging at a constant rate of C/5, where C is the charge.[693,694] However, this initial amount of extracted lithium cannot be reversibly reinserted and a material with the composition Li$_{0.85}$NiO$_2$ is formed at the end of the first discharge. Lithium deinsertion from this material is highly reversible during subsequent charge/discharge cycles. Thus, the reversible electrode reaction in the potential range from 2.5 to 4.1 V vs. Li/Li$^+$ can be described by Equation 5.[694]

$$Li_{0.35}NiO_2 + 0.5\ Li^+ + 0.5\ e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Li_{0.85}NiO_2 \quad (5)$$
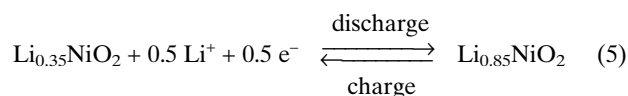
Lithium can move in Li$_x$NiO$_2$ in between the NiO$_2$ layers via a vacancy diffusion mechanism. The chemical diffusion coefficient for lithium can reach up to 2×10^{-11} m^2/s for Li$_{0.95}$NiO$_2$. At this composition the lithium mobility is very high.[695]

Unfortunately, several problems arise during the synthesis of the layered LiNiO$_2$ at temperatures above 600 °C, which are necessary to complete the oxidation from Ni^{2+} to Ni^{3+} in oxygen atmosphere and to obtain a sufficiently high degree of crystallinity. The existence of a broad phase width $0 \leq y < 0.4$ in Li$_{1-y}$Ni$_{1+y}$O$_2$ implies structural and compositional varieties of the same phase that strongly depend on the synthesis conditions. Due to the volatility of Li$_2$O at elevated temperatures, any known thermal treatment of LiNiO$_2$ leads to a decrease in the lithium oxide content. The resulting lithium-deficient compositions Li$_{1-y}$Ni$_{1+y}$O$_2$ have a partially disordered cationic distribution at the Li sites. This defect structure is considered to be responsible for the gradual breakdown of the oxide structure during repeated lithium insertion/deinsertion cycles, and leads to a diminishing of the specific charge during cycling of the LiNiO$_2$ electrode.[696–698] At temperatures above 850 °C the rhombohedral LiNiO$_2$ decomposes completely to the electrochemically inactive Li$_z$Ni$_{1-z}$O ($0 < z < 0.3$) which has a NaCl-type structure with a fully disordered cationic distribution.[659,699,700]

Several optimized preparation procedures have been suggested to achieve the stoichiometric composition LiNiO$_2$ with the two-dimensional structure that is considered to have the best electrochemical performance.[698,700–707] Typically, an excess of a lithium precursor (e.g., LiOH or LiNO$_3$) is heated with a nickel compound (e.g., Ni(OH)$_2$ or Ni(NO$_3$)$_2$) at temperatures between 600 °C and 800 °C in a stream of oxygen. The oxygen atmosphere suppresses the decomposition reaction of LiNiO$_2$ to Li$_{1-y}$Ni$_{1+y}$O$_2$ and Li$_z$Ni$_{1-z}$O$_{1+y}$O$_2$ at high temperatures.[700] The Li$_{1-y}$Ni$_{1+y}$O$_2$, in which y is close to 0 and the oxidation state of nickel is >2.95, has been prepared from LiOH and NiO at temperatures up to 700 °C in air and tested in prototype LiNiO$_2$/carbon cells between 2.5 and 4.1 V vs. Li/Li$^+$.[694] 1200 cycles with a 60 % retention of the capacity have been
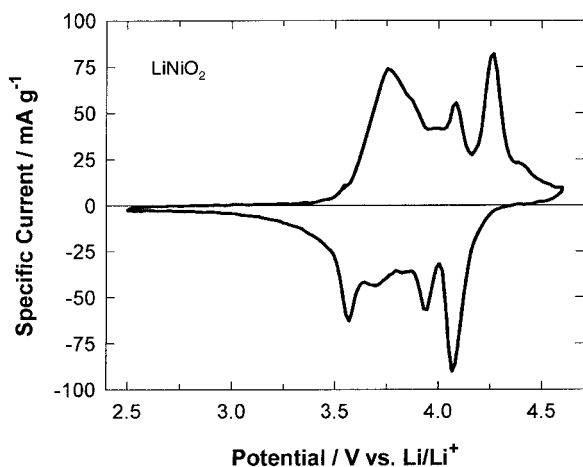
demonstrated and both the structure and the texture of the $LiNiO_2$ were found to be maintained.

Besides the synthetic optimization of the $LiNiO_2$, substitution of 30 mol.-% of the nickel in $LiNiO_2$ with cobalt has been shown to lead to an almost strictly 2D structure with a supreme electrochemical performance.[708] The cobalt stabilizes the layered structure. This is manifested by an increase of the trigonal distortion of the cubic oxygen array with increasing cobalt content.[709] Doping the $LiNiO_2$ with elements such as Co, Mn,[710–713] B,[710] and Al[710,714–716] has also been applied to limit the various phase transitions occurring while deinserting lithium from $LiNiO_2$.

Independent investigations in several laboratories of undoped $LiNiO_2$[697,702,717] have shown the existence of a hexagonal, a monoclinic, and two other hexagonal phases while decreasing the lithium content from $x = 1$ to $x = 0$. Passing the first three phases during the electrochemical oxidation, the interlayer distance between the NiO_2 sheets expands almost continuously from ca. 4.73 Å to ca. 4.8 Å as x in Li_xNiO_2 approaches 0.5, where it levels off until $x < 0.25$. The electrode rechargeability in this stoichiometry range is reported to be excellent.[694,717,718] Further oxidation leads to a two-phase region with the layered hexagonal NiO_2 as one of the components, in which the interlayer distance is reduced. Reinsertion of lithium into this compound is difficult, leading to a bad reversibility of Li_xNiO_2 at potentials positive of 4.2 V vs. Li/Li$^+$. An overcharging to $x < 0.25$ can be avoided by the use of solid solutions of $LiNiO_2$ containing 25 mol.-% of the isostructural but electrochemically inactive $LiAlO_2$. The $LiAl_{0.25}Ni_{0.75}O_2$ deinserts lithium in a single-phase region until the insulating composition $Li_{0.25}Al_{0.25}Ni_{0.75}O_2$ is formed, from which no further lithium can be deinserted electrochemically.[716]

The solid solution $LiNi_{0.5}Co_{0.5}O_2$ is also claimed to deinsert lithium in a homogeneous phase.[693] A redox potential slightly more negative than $LiCoO_2$ and $LiNiO_2$ and a specific charge of about 130 Ah/kg make this insertion compound a promising electroactive material.

LiVO₂: Unlike $LiCoO_2$ and $LiNiO_2$, the layered structure of $LiVO_2$ is destabilized by lithium deinsertion. At $x = 0.3$ in Li_xVO_2, approximately one third of the vanadium ions migrate from the vanadium layer to the lithium-depleted layer.[719] This process destroys the two-dimensional space for lithium diffusion and results in a defect rock-salt structure, which offers only limited electrochemical activity.[720]

Layered Manganese Oxides: Among the electrode materials with the composition $LiMO_2$, the lithium manganese oxide $LiMnO_2$ would be the most attractive for ecological and economical reasons. A layered $LiMnO_2$ with the α-$NaFeO_2$ structure has not been directly prepared yet. However, the lithiation of δ'-MnO_2 with lithium iodide leads to $Li_{1.09}Mn_{0.91}O_2$ with a layered structure that closely resembles the α-$NaFeO_2$ type but has an excess of lithium in the manganese layers.[721] The material discharges in the 3 V region. Unfortunately, the oxygen arrays in the structure

are unstable upon lithium extraction, which limits the use of this compound as a secondary electrode material. δ'-MnO_2 itself is regarded as a layered material with sheets of edge-shared MnO_6 octahedra and alternate layers of empty trigonal prisms. It can be synthesized using acid leaching of Li_2MnO_3, resulting in $Li_{2-2x}MnO_{3-x}$ ($0 < x \leq 1$) with some residual Li$^+$ ions and ion-exchanged H$^+$ ions. Extensively delithiated $Li_{2-2x}MnO_{3-x}$ is thermally unstable. The capacity loss observed during successive lithium insertion/deinsertion has been attributed largely to some residual water still associated with the structure.[721–723]

LiMnO₂: The thermodynamically stable phase with the composition $LiMnO_2$ crystallizes in the orthorhombic space group *Pmmn*.[724] Its structure could be described as a modified rock-salt type with a distorted cubic close-packed oxygen anion array. The lithium and manganese cations occupy the octahedral interstitial sites in such a way that alternating zig-zag layers of edge-sharing [LiO_6] and [MnO_6] octahedra are generated, as illustrated in Figure 19. Although the structure can be described as layered, it differs from the layered structure of $LiNiO_2$ and $LiCoO_2$, in which alternating [$LiO_{6/3}$] and [$Co(Ni)O_{6/3}$] planes lie parallel to each other (cf. Fig. 17).
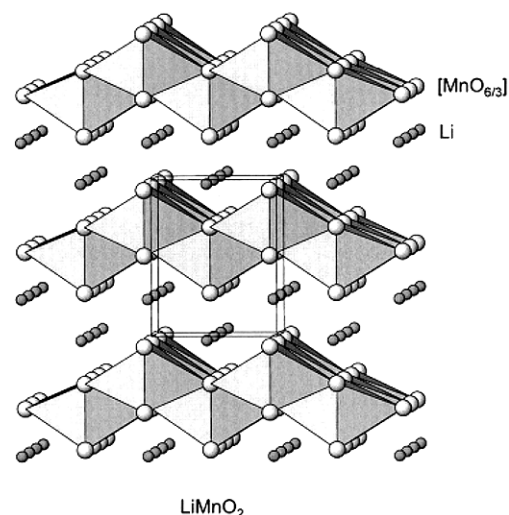
Fig. 19. The two-dimensional crystal structure of $LiMnO_2$.

Orthorhombic $LiMnO_2$ material synthesized from Li_2O and Mn_2O_3 at 750 °C under inert gas atmosphere does not show sufficient electrochemical activity in lithium cells. However, a report by Ohzuku et al.[725] showed that a predominantly orthorhombic $LiMnO_2$ product, prepared by heating an equimolar mixture of γ-$MnOOH$ and $LiOH$ below 450 °C, is electrochemically active. It delivers a specific charge of 190 Ah/kg in the potential interval between 2.0 V and 4.25 V vs. Li/Li$^+$. Various synthetic methods have been suggested in the meantime,[725–734] leading to materials with a similar electrode performance. However, all the $LiMnO_2$ materials suffer from a limited cycling stability. In the final stages of the delithiation process, $LiMnO_2$ transforms irreversibly into a spinel-type structure.[726] Thus, on cycling, the

orthorhombic $LiMnO_2$ component transforms gradually into a tetragonal lithiated spinel compound, which is responsible for the poor cycleability of the electrode.[726,727,730]

Other forms of layered $LiMnO_2$ have been prepared by the ion-exchange reaction of $NaMnO_2$ in Li^+-containing salt melts[735] or LiCl (LiBr)/*n*-hexanol.[736] The monoclinic $LiMnO_2$ resulting from the latter method could electrochemically deinsert up to 0.95 Li^+ per formula unit, corresponding to 270 Ah/kg. In a potential range between 3.4 V and 4.3 V vs. Li/Li^+ a specific charge of about 200 Ah/kg could be obtained.[736] Although this material still suffers from a limited cycleability, there are good chances that a further optimization may yield satisfactory results.

3.3. Three-Dimensional Hosts

Three-dimensional framework structures have cross-linked channels allowing ion insertion. The size of the channels must be sufficiently large to accommodate the ions. The advantage of three-dimensional frameworks over two-dimensional layered structures is: i) the possibility of avoiding, for steric reasons, the co-insertion of bulky species such as solvent molecules; and ii) the smaller degree of expansion/contraction of the framework structure upon lithium insertion/deinsertion.

3.3.1. Manganese Oxides

Manganese oxides are among the most popular positive electrode materials in primary lithium batteries due to their high abundance, low cost, favorable charge density, rather high electronic conductivity, and suitable electrode potential. Out of the various structurally defined binary manganese(IV) oxides (α-MnO_2 (hollandite structure type, (1×1) and (2×2) tunnels),[723,737–746] β-MnO_2 (rutile structure type, (1×1) tunnels),[723,737–739,747–749] ramsdellite-MnO_2 (ramsdellite structure type, (1×2) tunnels),[723,737–739,750–753] γ-MnO_2 (intergrowth of rutile/ramsdellite[754] (1×1) and (1×2) tunnels),[723,737–739,741,743,750,755–760] δ-MnO_2 (layered structure),[721–723,737,761,762] and λ-MnO_2 (spinel structure type)[763,764]) so far only γ-MnO_2 and λ-MnO_2 have gained importance in lithium battery technology. Electrolytic manganese dioxide (EMD) and chemical manganese dioxide (CMD) belong to the γ-group, which is used as battery grade manganese oxide in primary lithium cells. These oxides are intrinsically reversible to lithium insertion. However, a large expansion of the lattice occurs in γ-MnO_2 even at low depths of discharge, leading to structural collapse during cycling.[765,766] To stabilize the γ-MnO_2, Sanyo Electric Co. has developed a composite dimensional manganese oxide (CDMO) with a considerably improved reversibility.[723,737,767–777] It is prepared by reacting γ-MnO_2 with LiOH or $LiNO_3$ (Li:Mn = 3:7) at 370 °C, leading to a mixture of non-stoichiometric spinel phase and a lithiated phase derived from γ-MnO_2. The reversibility of

CDMO was attributed to the presence of the spinel phase, which plays the dominant and vital role in stabilizing CDMO electrodes and in their good electrochemical properties.[773,774,776]

The oxide λ-MnO_2 ($[Mn_2]O_4$) represents the host spinel framework that results from the stoichiometric spinel phase $LiMn_2O_4$ by completely extracting lithium (chemically in an acid or electrochemically).[763,764,778] Besides $LiNiO_2$ and $LiCoO_2$, the lithiated spinel $LiMn_2O_4$ is at present a very popular lithium-containing positive electrode material.[78,468,473,779–781] Its cubic spinel structure, shown in Figure 20, can be described as a cubic close-packed oxygen array with the oxygen anions on the crystallographic 32e sites of the *Fd3m* space group. The manganese cations occupy half of the octahedral interstitial sites, 16d, and the lithium cations one eighth of the tetrahedral sites, 8a. The interstitial space in the $[Mn_2]O_4$ framework represents a diamond-type network of tetrahedral 8a and surrounding octahedral 16c sites. These empty tetrahedra and octahedra are interconnected with one another by common faces and edges to form 3D diffusion pathways for Li^+ ion diffusion.[782] Chemical diffusion coefficients in the range 10^{-12} to 10^{-14} m^2/s could be obtained, depending on the synthesis conditions and measurement technique.[783–785]
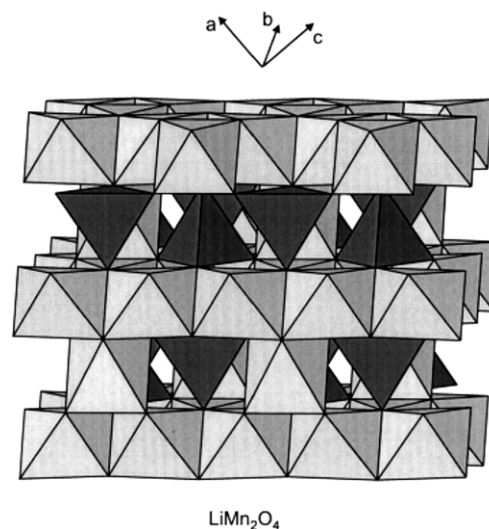
Fig. 20. The three-dimensional crystal structure of $LiMn_2O_4$.

The electrochemical Li^+ deinsertion from the tetrahedral sites of $LiMn_2O_4$ is reversible and proceeds at about +4 V vs. Li/Li^+.[786–789] This process is represented by the peaks 2 and 3 in the typical cyclic voltammogram of $LiMn_2O_4$ shown in Figure 21. The two-step process indicates a phase transition at $Li_{0.5}Mn_2O_4$, which is ascribed to an ordering of lithium on the tetrahedral 8a sites. During charging and discharging in the "4 V" potential range the cubic symmetry of the structure is maintained.[790] The good rechargeability and cycling stability of $LiMn_2O_4$ is attributed to the fact that Li^+ is deinserted from the cubic structure with a minimal contraction of the unit cell over a wide composi-
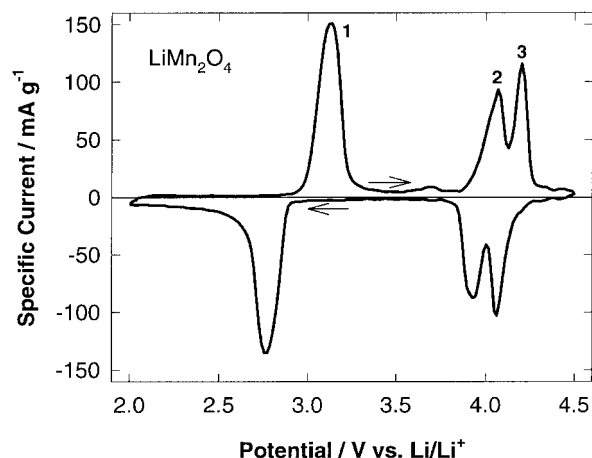
Fig. 21. The cyclic voltammogram of LiMn$_2$O$_4$.

tion range. However, at practical potentials ($\ll$5 V vs. Li/Li$^+$) it is not possible to extract all the lithium electrochemically and form λ-MnO$_2$.

It is also possible to insert additional Li$^+$ in the empty octahedral 16c sites of LiMn$_2$O$_4$. The electrochemical insertion/deinsertion occurs at about +3 V vs. Li/Li$^+$ (the corresponding peak pair is labeled 1 in the cyclic voltammogram in Fig. 21)[782,789,791] but the cycling performance is rather poor. The poor cycling behavior of Li/LiMn$_2$O$_4$ cells in the "3 V" voltage range is attributed to an asymmetric lattice expansion/contraction of the Li$_{1+z}$Mn$_2$O$_4$ electrode during discharge/charge reactions. This lattice distortion is largely a result of the Jahn–Teller effect of the Mn^{3+} ion. This effect transforms the cubic crystal symmetry of the spinel electrode into tetragonal symmetry.[782,789,791,792] Thus, charging and discharging in the "3 V" potential range typically proceeds in a two-phase region consisting of the cubic and tetragonal spinel within a nominal composition range of $0.1 < z < 0.8$ in Li$_{1+z}$Mn$_2$O$_4$.[790,793] The electrochemical performance in the "3 V" potential window can be significantly improved by decreasing the amount of Mn^{3+} in the spinel compound. Mean oxidation states higher than 3.5 can be found for manganese in defect spinel compounds with nominal compositions Li$_2$O·yMnO$_2$ ($2.5 \leq y \leq 4$), which exhibit higher specific charges and better cycling stabilities in the "3 V" region than materials with the ideal spinel composition.[794–798] However, for use as a "3 V" electrode material in a cell with a carbon counterelectrode the oxides would have to be chemically lithiated.

The electrochemical performance in the "4 V" potential region of stoichiometric spinels LiMn$_2$O$_4$ strongly depends on the method of their preparation, especially the choice of the starting materials for the solid-state reactions and the heat treatment conditions. These parameters are especially important to achieve a high crystallinity, to avoid phase impurities, and to adjust the correct oxygen stoichiometry.[799–821] By introducing a new electrolyte system compatible up to +5 V vs. Li/Li$^+$ with the LiMn$_2$O$_4$ positive elec-

trode, Tarascon and Guyomard made a decisive step towards the commercialization of LiMn$_2$O$_4$/carbon cells.[471,473,476,780] However, on long term cycling, even optimized cells have turned out to show a slight capacity fading.[809] This fading is attributed to the instability of the organic-based electrolyte at the very high voltages reached when charging the cells, resulting in the slow dissolution of the Li$_x$Mn$_2$O$_4$ electrode in the electrolyte (Mn^{2+} is a soluble species that is produced from Mn^{3+} by the disproportionation reaction to Mn^{2+} and Mn^{4+}), as well as to an onset of the Jahn–Teller effect in deeply discharged Li$_x$Mn$_2$O$_4$ electrodes (i.e., at $x \approx 1$).[822] Replacing some manganese in LiMn$_2$O$_4$ with mono- or multivalent cations (e.g., Li$^+$, Mg^{2+}, or Zn^{2+}) or, alternatively, doping the oxide with additional oxygen increases the average manganese-ion oxidation state slightly above 3.5, suppresses the Jahn–Teller effect on deep discharge, and leads to an improved rechargeability of the oxide.[822] Other approaches have been the substitution of the Jahn–Teller ion Mn^{3+} by other trivalent cations (Al^{3+}, Fe^{3+}, Ni^{3+}, Co^{3+}, or Cr^{3+}).[74,823–826] However, all the reported doping methods have led to a decreased specific charge compared to the undoped LiMn$_2$O$_4$ materials so far.

3.3.2. Other Spinels

Binary spinel compounds such as Mn$_3$O$_4$, Fe$_3$O$_4$, and Co$_3$O$_4$ have only gained subordinate consideration as lithium insertion materials so far. In these lithium-free compounds the bulky cations on the 8a sites impede Li$^+$ ion diffusion.[782,786,789,791] This might be the reason why usually only lithium-containing spinel oxides are used.[802,821] The wide range of transition-metal ions that can be stabilized on the octahedral 16d sites of the framework in lithium-containing spinels give the possibility of tailoring the redox potential of the oxides, synthesizing, for example, LiMnVO$_4$[827] or LiNiVO$_4$[828] (a "4.8 V" electrode material). Also Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ reversibly inserts about one Li$^+$ per formula unit without remarkable strain in its structure, in this case at about +1.5 V vs. Li/Li$^+$.[829] Combined with a lithium-containing "4 V" oxide, Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ is discussed as a negative electrode in an all-oxide lithium ion cell.[779,781,829–831]

3.3.3. Vanadium Oxides

Highly oxidized oxides of vanadium, chromium, niobium, as well as molybdenum are well known for their ability to electrochemically insert large amounts of lithium.[3,645,832–843] However, mostly due to a limited cycling stability, so far only the vanadium oxides V$_2$O$_5$ and V$_6$O$_{13}$ have gained importance as rechargeable "3 V" electrode materials. The structures of the two vanadium oxides are shown in Figure 22.

The oxide V$_2$O$_5$ forms layers of edge- and corner-sharing VO$_5$ square pyramids.[844,845] The apical vanadium–oxygen
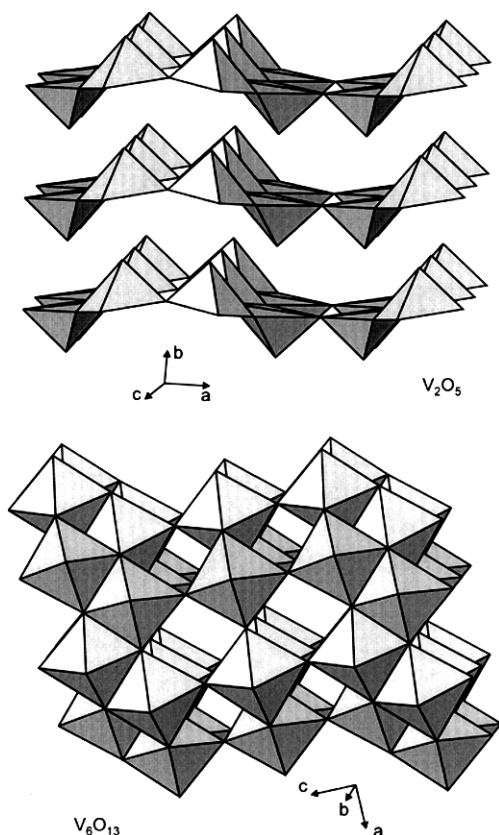
Fig. 22. The crystal structures of V_2O_5 and V_6O_{13}.

bond distance is much shorter than the four other distances and corresponds to a double bond, as shown by the infrared absorption frequency.[846,847] Although such a description illustrates the two-dimensional character of this material, it is also possible to describe the structure of V_2O_5 as distorted VO_6 octahedral, which emphasizes the structural relationship to ReO_3 via crystallographic shears.[5,848,849] The very large length of the sixth vanadium–oxygen bond underlines the structural anisotropy of this material and the ability to insert guest species in perovskite-like cavities. Also the V_6O_{13} structure can be described as a shear structure derived from the ReO_3 and the V_2O_5 structures.[5,850,851] As the V_2O_5 lattice shears to the lower state vanadium oxide, V_6O_{13}, edge sharing of the $[VO_6]$ octahedra increases and the framework strengthens.

After Whittingham reported the reversible electrochemical lithium insertion into V_2O_5 at room temperature in 1975,[629] it was believed for a long period of time that V_2O_5 is very sensitive to overdischarge: a lithium content of $x = 1$ in $Li_xV_2O_5$ cannot be exceeded without losing the reversibility of the insertion process.[360,846,852–858] Depending on the amount of inserted lithium several structural modifications were observed: α- and ε-phases exist for $x < 0.01$ and $0.35 < x < 0.7$ in $Li_xV_2O_5$, respectively,

exhibiting a V_2O_5-type structure with increasing puckering of the layers.[846,852,859,860] For the composition LiV_2O_5 gliding of one layer out of two leads to the δ-phase.[860] These phase transitions are fully reversible and the pristine V_2O_5 phase is recovered upon lithium deinsertion.[861] However, for a lithium content $x > 1$ the δ-phase is irreversibly transformed via a reconstruction mechanism, leading to a structural modification related to the γ-phase.[859] It was shown in 1989 that the resulting γ-phase can be reversibly cycled in the stoichiometric range $0 \leq x \leq 2$ under retention of the γ-type structure.[859,862–865] Further insertion of a third lithium into V_2O_5 leads to the irreversible formation of the so-called ω-phase with a rock-salt type structure. The latter can be prepared either chemically using an excess of butyl lithium or electrochemically at a potential of about 1.2 V vs. Li/Li+.[865–869] Almost all the lithium from the ω-phase can be electrochemically deinserted again, leading to a unique positive electrode material for secondary lithium batteries for which a specific energy of up to 900 Wh/kg can be obtained. 100 cycles with more than 450 Wh/kg have been demonstrated for a ω-$Li_xV_2O_5$/Li cell in a voltage range between 3.4 V and 1.9 V.[865,869]

Besides crystalline V_2O_5, rather promising results have been reported for V_2O_5 glasses with P_2O_5 or other network formers,[360–365] V_2O_5 xerogels,[870–876] and V_2O_5 aerogels.[877] These amorphous or low-crystalline materials offer considerable advantages by virtue of their morphology. A large electrochemically active surface area, small particle size, and low density provide both high overall diffusion coefficients and low volume expansion during lithium insertion. Specific energies of over 700 Wh/kg were measured for lithium cells with a xerogel positive electrode.[871] However, limited long-term cycling stability is a major problem of such electrode materials at present.

V_6O_{13} was first reported as a positive electrode material by Murphy et al.[878,879] Up to eight Li+ ions per formula unit can be chemically inserted into stoichiometric V_6O_{13} using butyllithium, and even more can be inserted into non-stoichiometric V_6O_{13+z}.[880] However, only up to six Li+ ions can be reversibly inserted into V_6O_{13} electrochemically.[881] In-situ X-ray diffraction during electrochemical Li+ insertion revealed four phases, identified as $Li_{0.5}V_6O_{13}$, $Li_{1.5}V_6O_{13}$, $Li_3V_6O_{13}$, and $Li_6V_6O_{13}$, which were also observed during chemical insertion studies.[882] The lithium diffusion coefficient ranges from 3×10^{-13} to 8×10^{-14} m²/s.[880,883] Practical problems of the rechargeable V_6O_{13} electrode are a capacity loss during cycling, a high electronic resistivity of lithiated V_6O_{13},[880,884] and a relatively high lattice expansion of ~15 %, observed when x tends to six in $Li_xV_6O_{13}$.[880,885–889] Possible solutions to these problems that lead to fairly promising results are the use of: i) thin film electrodes[882,883,887] and ii) a suitable electronically conductive matrix in which the V_6O_{13} particles are embedded.[890]

The vanadates $Li_{1+x}V_3O_8$,[130,891–906] $Na_{1+x}V_3O_8$,[643,906] and $Mg(V_3O_8)_2$[144,147] are examples of insertion compounds in which the alkaline or alkaline-earth metal atoms function as pillars between the vanadium oxide units. They stabilize the oxide structure during the insertion/deinsertion process and optimize the space between the vanadium oxide units. This enhances not only the amount of insertable guest species but also the lithium diffusion rate, both leading to a superior electrode performance. The monoclinic structure of $Li_{1+x}V_3O_8$ and $Na_{1+x}V_3O_8$ illustrated in Figure 23 shows distorted $[VO_6]$ octahedra that are connected via shared edges and vertices to form $[V_3O_8]^-$ units. These units are stacked one on top of the other to form quasi-layers. The alkali metal ions are situated between these layers, electrostatically holding the $[V_3O_8]^-$ units together.[907,908] The spacing between the strands is sufficiently flexible to accommodate other guest species on octahedral and tetrahedral interstitial sites.[893] X-ray diffraction showed only a slight lattice expansion upon lithiation and no major structural changes even on long-term cycling for $Li_{1+x}V_3O_8$[887,893,894,897] and $Li_xNaV_3O_8$,[643,909] thus providing evidence of the strongly topochemical nature of the insertion process.
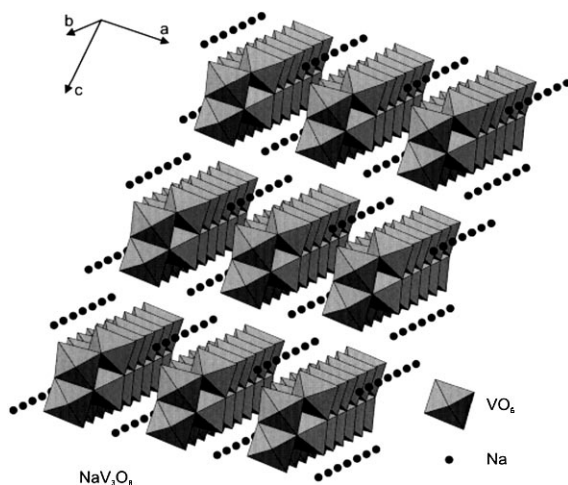

Fig. 23. The crystal structure of NaV_3O_8.

A specific charge for lithium insertion of more than 300 Ah/kg has been reported for these compounds.[643,893,909] The lithium diffusion coefficient ranges from 10^{-12} to 10^{-14} m^2/s.[643,893,894,897,901] Chemical lithiation leading to compositions $Li_{3.8}V_3O_8$[893,895] and $Li_3NaV_3O_8$[909] allows the use of these positive electrode materials as the lithium source in cells containing a carbon negative electrode. A stable specific charge of 210 Ah/kg has been demonstrated for more than 100 cycles with $Li_3NaV_3O_8$[909] (Fig. 24).

3.3.4. Complex Framework Structures

Recently, lithium iron phosphates and sulfates were shown to be good candidates for positive electrode materials. $Li_xFe_2(SO_4)_3$,[910] $Li_3Fe_2(PO_4)_3$,[911] $Li_3V_2(PO_4)_3$,[911]
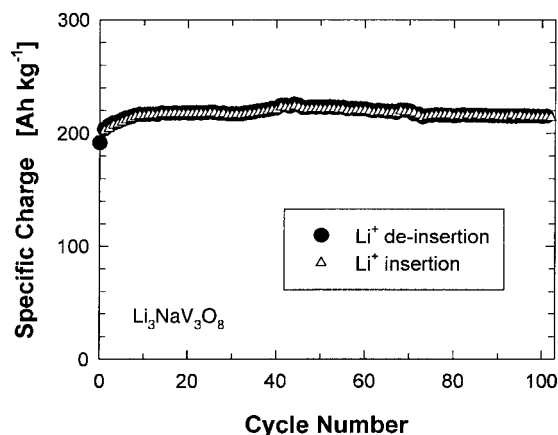
Fig. 24. The cycling stability of $Li_3NaV_3O_8$. The specific charge of $Li_3NaV_3O_8$ was measured galvanostatically between 1.5 and 4.0 V vs. Li/Li$^+$.

$Li_3FeV(PO_4)_3$,[911] and $Li_2FeTi(PO_4)_3$[912] belong to the family of compounds with an open Nasicon framework structure; $LiFePO_4$ and $FePO_4$ are phospho-olivines.[913] These polyanion-containing compounds show reversible electrochemical lithium extraction/insertion in an interesting potential region between 3 V and 3.5 V vs. Li/Li$^+$ as well as high lithium diffusion rates. Additionally, they are inexpensive, non-toxic, and environmentally benign. Although the specific charges are relatively low (ca. 100 Ah/kg), these compounds might point to a new direction in solid-state electrochemistry for advanced battery materials.

4. Li$^+$ Ion Transfer Cells

In the last few years various rechargeable lithium systems have been developed but only a few of them have been successfully commercialized.[7,52,59,80,202,353,914,915] Nowadays, lithium ion transfer cells dominate development in this sector, and the commercial interest in lithium ion transfer systems grows continuously. This is because the Li$^+$ ion transfer battery is a very promising system for satisfying the demand for high specific energy and high power batteries for portable applications, especially for cellular phones and portable computers. Moreover, from a comparison with other systems (Fig. 25) it is clear that the lithium ion transfer battery is a worthy candidate for energy storage in electric vehicles.[75,113,916–920]

In Li$^+$ ion transfer cells (Fig. 26) both electrodes are capable of reversible lithium insertion. Because of the difference in chemical potentials of lithium in the two electrodes, the transfer of lithium ions from the negative electrode through the electrolyte into the positive electrode (discharge) delivers energy, whereas the reverse lithium transfer (charge) consumes energy. For practical cells, carbon-based negatives and metal oxide–based positives have been selected, as they can provide maximum specific energy, sufficient specific power, and long cycle life.[7,52,59,62,63,75,921–925]
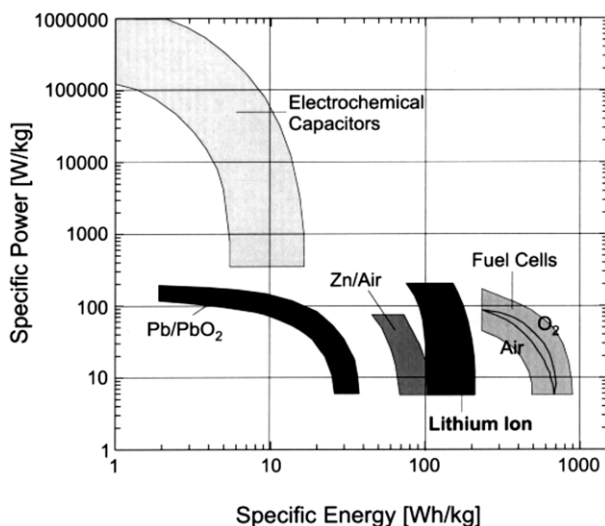
ADVANCED MATERIALS

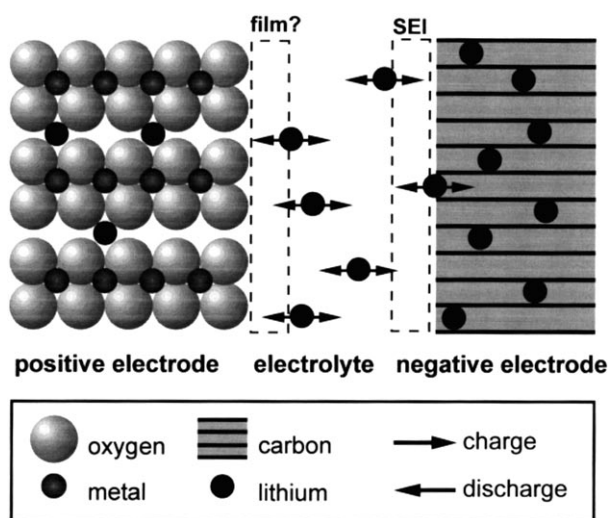Fig. 25. Ragone plot of some electrochemical energy storage/conversion systems.

Fig. 26. Schematic representation of a Li⁺ ion transfer cell.

Liquid organic electrolytes are typically found in commercially available cells.

At present, four positive electrode materials are favored: $LiCoO_2$,[79,83,84] $LiNiO_2$,[694,718,926] $LiMn_2O_4$,[468,469,473–476,925,927] and V_2O_5.[81,401,928] Three of them are lithiated "4 V" oxides. They allow cell manufacture in the discharged state with the positive electrode as lithium source for the carbon negative. The electrodes are scarcely air sensitive. In the case of V_2O_5 a lithium metal laminate is attached to the carbon negative electrode. After filling in the electrolyte, the metallic Li reacts with carbon and forms Li_xC_6, which is then the lithium source in the cell. However, the use of moisture- and air-sensitive lithium metal complicates the cell assembly and there is also a safety uncertainty since residual metallic lithium might remain in the cell even during cycling. Thus, this ion transfer system has found only limited application in small coin cells.[81,401,923,928]

4.1. Construction of Li⁺ Ion Transfer Cells

Mass transport limitations generally worsen the utilization and rate capability of electroactive materials and, thus, the specific energy and power of batteries. This is especially true for lithium insertion materials where lithium transport is hindered by the rather slow transport kinetics of lithium from the bulk to the surface of the electroactive material particles.[7,59,80,200,289,291,376,803,929–937] Insertion electrodes are hence preferably fabricated as thin films from small particle size (~5 to ~30 μm) electroactive materials.[7,202,278–280,929–931,935,938–949] There are activities to develop very thin, all-solid-state microbatteries using vapor-phase deposition techniques.[103,106,110,961,962] The prevailing industrial methods to produce thin electrodes for lithium ion transfer cells, however, are coating processes known from the manufacture of magnetic tapes.[13,52,59,79,83,84,200,925] Thin composite porous layers (~60 to ~90 μm) of the electroactive material (oxide or carbon) with a few percent of a polymer binder (to adjust the mechanical properties of the layer) are coated on both sides of a current collector. The current collector is usually a 20 μm thick Al foil for the positive electrode and a copper foil of the same thickness for the negative electrode. In addition, the metal oxides contain about 10 % of an inert material, ensuring electronic conductivity (e.g., graphite). The composite electrodes are separated by thin microporous separators. The thickness of the whole package (Fig. 27) is typically about 400 μm. In the Sony 18650 cylindrical cell (18 mm diameter and 65 mm height),[83,84] for example, the electrode laminate is ~50 cm long and 5.4 cm wide.[200] The laminate is in this case spirally wound. It is placed into a cylindrical metal can before a liquid electrolyte is filled in.

The use of a polymer electrolyte instead of a liquid one offers several advantages in cell assembly.[50,51,114–122,275,963–970] The polymer electrolyte is used both as a binder and as a separator. Batteries with an enormous shape flexibility can be designed where a conceivable leakage of the liquid electrolyte is avoided. According to this concept a "plastic" lithium ion transfer technology has been developed at Bellcore. Their cell uses a "wet" hybrid electrolyte, which is actually not a true polymer electrolyte but an inert polymer containing an immobilized liquid electrolyte.[123–126,971,972]

One or more formation charge/discharge cycle(s) are generally performed after the assembly of lithium ion transfer cells. During the first cycle(s) an SEI film is formed on the negative carbon electrode and, possibly, interface or film effects also occur on the positive electrode (Fig. 26). The film formation irreversibly consumes charge. The practical specific energy of formed cells is therefore only 80–90 % of that corresponding to the mass of the

built-in electroactive materials. Of course, a careful adjustment of the balance of negative to positive electrode material masses is required to reach maximum performance.[125,220,470,472,473,525,830,925,973,974] Due to a moderate self-discharge (typically <10 % per month at room temperature) the originally charged cells arrive at the consumer in an undefined condition. The self-discharge reactions are partly irreversible due to electrolyte decomposition. However, a satisfactory explanation of the self-discharge mechanism is still not available.[59,79,83,84,123,155,470,472,925,975–978]

In contrast to the beneficial effect of small particle size (high specific surface area) on the specific power, numerous investigations have proved that an increased specific surface area of the electroactive particles negatively influences the safety characteristics, the charge losses, and the cycling performance of ion transfer cells.[80,200,378,382, 428,597,979–984] This is primarily because the extent of electrolyte decomposition is coupled with the electrode surface wetted by the electrolyte.[428,469,980,985–987] The manufacture pressure for electrode preparation is also crucial.[980,985,988] Low manufacture pressures usually give higher electrode porosity but rather poor contacts between the particles. At high manufacture pressures the electrode porosity is low and hence the electrode is insufficiently wetted by the electrolyte. Moreover, in low-porous electrodes variations in volume of the individual particles during lithium insertion and deinsertion induce mechanical stress between the particles, that is, in the entire composite electrode.[278,337,989] For optimum performance the electrode porosity should be precisely adjusted, for example, by the use of pore-forming additives.[988] Mathematical modeling techniques can be used for electrode and cell optimization.[929-931,990–1017]

4.2. Safety of Li⁺ Ion Transfer Cells

Rechargeable Li⁺ ion transfer batteries with a negative insertion electrode are considered to be considerably safer than rechargeable batteries containing metallic lithium. Of course, the redox potential of lithium-rich Li_xC_6 compounds is rather close to that of metallic lithium (Fig. 8) and the reactivity of both is similar. The particle size of Li_xC_6 in battery electrodes is typically of the order of ~10 μm. The reactive surface area is therefore large. Moreover, recent investigations have shown that cycling of graphite electrodes increases the specific surface area of Li_xC_6 by a factor of five.[985] However, the reaction rate of Li_xC_6 is limited by the rather slow transport kinetics of lithium from the bulk to the surface of carbon particles.[219–221] Even more important is that the melting point of Li_xC_6 is incomparably higher than that of metallic lithium (about 180 °C). Therefore, there is no risk of a hazardous breakdown of the protective SEI layer, which happens during accidental melting of metallic lithium electrodes. However, it has to be considered that although elemental lithium is absent, significant exothermic reactions of the electrolyte may be initiated by application of heat.[419,1018]

An important safety-relevant issue of ion transfer cells is the interface between the electrolyte and the two electrodes. Conventional 4 V lithium ion cells operate far beyond the thermodynamic stability window of organic electrolytes, and electrolyte decomposition therefore occurs. Fortunately, electrolyte reduction products form a protective film at the negative electrode, which hinders further reduction. Whereas the occurrence of a protective SEI film on the negative electrode has been generally accepted, up to now there are only a few papers that report that the electrolyte oxidation does form a protective interface at the positive electrode.[79,130,176–179] The rate of electrolyte oxidation is extremely dependent on both the kind of electroactive material and on its state of charge.[220,419,1019] Positive electrode materials can even dissolve in the electrolyte to some extent.[820,1020–1022] Thus, the interface between the electrolyte and the positive electrode remains a major problem, in particular at the end of charge
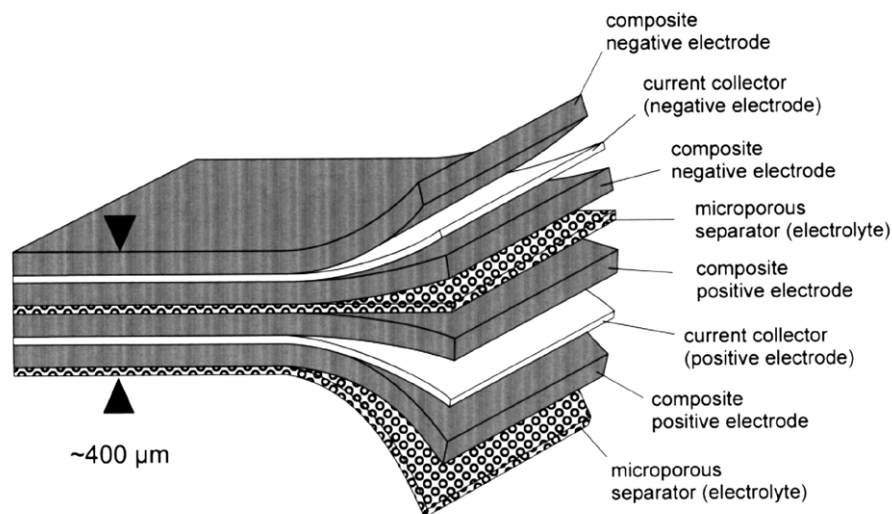
Fig. 27. Schematic representation of a Li⁺ ion transfer cell laminate.

~400 μm

composite negative electrode

current collector (negative electrode)

composite negative electrode

microporous separator (electrolyte)

composite positive electrode

current collector (positive electrode)

composite positive electrode

microporous separator (electrolyte)

and at elevated temperatures, when the electrolyte oxidation rate increases.[468–476,925,1019,1023]

Several tests and considerations identified the following safety-relevant issues of Li+ ion transfer cells:[79,83,84,219–221,470,509,510,975,1019,1024–1027] i) Fully charged, fairly delithiated positive electrode materials are strong oxidants. At temperatures above ~180 °C[220,1019] a hazardous thermal run-away of the cell may happen due to the thermal decomposition of the positive electrode material in combination with the strongly exothermic oxidation of the organic electrolyte. ii) At elevated temperatures the reactivity of the negative electrode also increases.[219,221,509] iii) Common electrolytes contain highly volatile and highly flammable low viscosity components such as dimethyl carbonate and dimethoxyethane. iv) Combustible and partly inflammable gaseous electrolyte decomposition products can accumulate in the ion-transfer cell during charging.[510]

The safety issues are even more important for larger cells and cell stacks. Because the lithium ion transfer cells do not tolerate overcharge and overdischarge, each individual cell in a battery is managed by an electronic surveillance and control system that also switches the current off under abuse conditions.

To enhance the safety of lithium ion transfer cells some approaches were tested, for example, built-in internal safety devices[79,83,84,1028–1033] and electrolyte components that are either more oxidation tolerant[476,925] or less flammable (e.g., fluorinated ethers[1034]). An interesting possibility is chemical overcharge/overdischarge protection by a redox shuttle mechanism. There are some examples of metallocene shuttles forming redox pairs MC/MC+. These were tested in "3 V" cells containing metallic lithium,[54,1035–1037] but suffered from insufficient long-term stability. The redox shuttles work as follows: They are dissolved in the electrolyte solution. When the overcharge potential is approached, MC is electrochemically oxidized at the positive electrode to MC+. The MC+ is transported by migration and diffusion to the negative electrode and reduced there to the starting material MC, which diffuses back to the positive electrode. However, whereas the surface of a metallic lithium electrode is periodically renewed during cycling, the carbonaceous negative electrode in a lithium ion transfer cell is passivated all the time by the SEI film. Thus, the reduction of MC+ and therefore the redox shuttle mechanism is hindered. Moreover, the potential of the soluble redox couple MC/MC+ must be more positive than the regular end-of-charge electrode potential. In a 4 V system this would be at least 4.3 V vs. Li/Li+!

5. Summary and Outlook

Both the performance and the safety of rechargeable lithium batteries strongly depend on the materials employed. Nowadays, rechargeable lithium batteries are essentially based on insertion electrodes. The present practice is to combine a "4 V" metal oxide ($LiCoO_2$, $LiNiO_2$, or $LiMn_2O_4$) with carbon (non-graphitic or graphite). The application of mixed or doped oxides is also promising. For economical and ecological reasons there is a trend towards manganese oxides. Because carbon is generally used as the negative electroactive material, lithium-free positive electrode materials such as V_2O_5 have only had limited success on the market. However, the possible introduction of lithiated negative electrode materials such as advanced lithium alloys could change the situation.

Carbonaceous electroactive materials are the state-of-the-art of the negative electrode. The first ion transfer cell commercialized by Sony used soft carbons with relatively low specific charge.[79,83,84] The increase in specific energy of the recent generation of ion transfer cells is particularly due to the use of carbons with higher specific charge (hard carbons and graphite). And still the future trends are directed towards higher specific charges and energy densities. In this respect, attention should be devoted to alternative negative electrode materials because the charge densities of certain Li alloys exceed by far that of carbon. The Fujifilm Celltech ion transfer cell, which uses an amorphous tin composite oxide as negative electrode material, shows energy densities higher than those of the competitors using carbons. Composite insertion materials also seem to be highly promising.[227,351,355,531,532,941,1038–1041] Besides the development of materials, technical improvements, for example, new electrode and cell designs, will also contribute to the rise of new generations of ion transfer cells.

At the present stage of development, lithium ion transfer batteries are available for portable electronic devices. Moreover, several companies have announced the appearance of electric cars equipped with large lithium ion transfer batteries before the end of this century.

[1] A common convention in the literature is that "intercalation" is regarded as a special case of "insertion". Nevertheless, occasionally both terms, insertion and intercalation, are used interchangeably. The term "intercalation" implies the restricting condition that a layered host matrix widely retains its structural integrity during the intercalation process. This is usually true for the insertion of lithium guest ions between the sheets of a host, for example, graphite or TiS_2. Less suitable is the term intercalation, for example, for the insertion of lithium into a metal matrix during formation of Li alloys because this process is associated with major structural rearrangements. In most cases, however, a strict differentiation between insertion and intercalation is only a formal question. In this review the term intercalation will only be used where the historical conventions or the present practice make its use appropriate. For further reading on the definitions and characterizations of insertion/intercalation reactions see, for example, [2–19].

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