The Structural Design of Electrode Materials for High Energy Lithium Batteries

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Lithium batteries are used to power a diverse range of applications from small compact devices, such as smart cards and cellular telephones to large heavy duty devices such as uninterrupted power supply units and electric- and hybrid-electric vehicles. This paper briefly reviews the approaches to design advanced materials to replace the lithiated graphite and LiCoO₂ electrodes that dominate today’s lithium-ion batteries in order to increase their energy and safety. The technological advantages of lithium batteries are placed in the context of water-based- and high-temperature battery systems.

Introduction

The first oil crisis in the mid 1970’s spawned intense R&D efforts to find alternative sources of energy and ways to store energy with the particular objective of lessening the dependence of the world’s transportation sector on fossil fuel supplies. Now, more than a generation later, despite the progress that has been made in discovering and developing new battery technologies for energy storage, such as molten salt, high-temperature sodium batteries, aqueous nickel–metal hydride batteries and non-aqueous, room-temperature lithium-ion batteries, further improvements and advances are essential in order to overcome the added concerns of growing CO₂ emissions and global warming.

The introduction of primary (non-rechargeable) lithium batteries in the 1970’s and, subsequently, secondary (rechargeable) ‘lithium-ion’ systems in the 1990’s to power portable electronic devices, created a revolution in battery technology and a marked swing away from the relatively low-voltage, water-based systems such as nickel–cadmium and nickel–metal hydride batteries, and high-temperature systems (Linden and Reddy, 2002). Because of their light weight and intrinsic high energy, lithium batteries offer the best opportunity for future progress over all known systems, as highlighted in a volumetric energy density vs. gravimetric energy density plot (Figure 1) and a comparison of theoretical capacities and energy densities of a few selected aqueous, high-temperature (molten salt) and lithium systems (Table 1). Lithium batteries are now being developed for a myriad of devices, both large and small, such as uninterrupted power supply units for the telecommunications industry and those required by the consumer electronics, medical, aerospace, defense and transportation sectors. The lithium battery industry now constitutes a ‘lithium economy’ that will continue to expand and grow significantly in the years to come, particularly with the introduction of hybrid-electric vehicles (HEVs), ‘plug-in’ hybrid-electric vehicles (PHEVs) and all-electric vehicles (EVs) powered by lithium-ion batteries.

Conventional 4 V lithium-ion cells, which are based on a LiₓC₆/Li₁–ₓCoO₂ electrochemical couple, provide high energy and power (Linden and Reddy, 2002). In their charged state, they are inherently unsafe. The lithiated-graphite electrode is strongly reducing, whereas a fully delithiated Li₁–ₓCoO₂ electrode is an extremely strong oxidant; in the presence of flammable organic electrolyte solvents, there is the risk of thermal runaway, cell venting, fire and explosion. Therefore, every LiₓC₆/Li₁–ₓCoO₂ cell in a battery pack needs to be protected by electronic circuitry to prevent overcharge. In this respect, much research has been conducted over recent years to find alternative electrode materials in the quest for safer lithium-ion batteries.

Although lithiated graphite remains the material of choice for the negative electrode (anode), considerable progress is being made to fabricate practical metal alloy or intermetallic electrodes that can store greater amounts of lithium. With respect to the positive electrode (cathode), the spinel LiMn₂O₄ (Thackeray et al., 1984a; Ohzuku et al., 1990) and its substituted derivatives (Gummow et al., 1994), and LiFePO₄ (olivine)
(Padhi et al., 1997) have also been commercialized in high-voltage lithium-ion cells. In practice, however, all three materials (LiCoO₂, LiMn₂O₄ and LiFePO₄) provide a relatively low electrochemical capacity at high potentials (3.5–4 V), thereby limiting the available energy of the lithium-ion cell. Recently, it has been demonstrated that lithium-rich, Li₂MnO₃-stabilized Li¹⁺ₓM¹⁻ₓO₂ electrodes in which M is predominantly manganese and nickel hold promise for increasing the capacity and energy of lithium-ion cells (Lu et al., 2002; Kim et al., 2004; Thackeray et al., 2005).

In this paper, the progress that has been made in developing alternative lithium battery materials is briefly reviewed; the importance of designing rechargeable electrodes from both a compositional and structural standpoint is highlighted. Technological advances and future opportunities are discussed in relation to other battery systems.

1. Insertion vs. Displacement Reactions

Electrochemical reactions take place, in general, either by insertion reactions or displacement reactions or a combination thereof. Insertion reactions occur when a guest ion, such as H⁺ or Li⁺, is accommodated within a host electrode structure. Well known examples of reversible insertion reactions are found in nickel–metal hydride- and lithium-ion batteries in which the H⁺ and Li⁺ ions are shuttled between the host structures of the metal (M) and graphite (C₆) anodes and the NiOOH and Li¹⁻ₓCoO₂ cathodes, according to reactions (1) and (2), respectively (Linden and Reddy, 2002):

\[ \text{MH} + \text{NiOOH} \leftrightarrow \text{M} + \text{Ni(OH)}₂ \]  
\[ \text{Li}^{x} \text{C}_₆ + \text{Li}_1⁻^x\text{CoO}_₂ \leftrightarrow \text{C}_₆ + \text{LiCoO}_₂ \]

The theoretical capacity of each electrode is determined by the number of electrons transferred during the electrochemical reaction. For reactions (1) and (2) above, a maximum of one electron can be transferred per transition metal ion in the NiOOH and Li¹⁻ₓCoO₂ electrodes, respectively, as shown in reactions (3) and (4) (Sudworth, 2001; Linden and Reddy, 2002):

\[ \text{MH} + \text{NiOOH} \leftrightarrow \text{M} + \text{Ni(OH)}₂ \]  
\[ \text{Li}_x\text{C}_₆ + \text{Li}_1⁻^x\text{CoO}_₂ \leftrightarrow \text{C}_₆ + \text{LiCoO}_₂ \]

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\[ \text{Pb} + \text{PbO}_₂ + \text{H}_₂\text{SO}_₄ \leftrightarrow 2\text{PbSO}_₄ + \text{H}_₂\text{O} \]  
\[ 2\text{Na} + \text{NiCl}_₂ \leftrightarrow 2\text{NaCl} + \text{Ni} \]
High-temperature Li/iron-oxide (Fe$_3$O$_4$, spinel) cells operate by combined lithium insertion/metal displacement reaction processes in the cathode to involve 2.33 electrons per iron atom (Thackeray et al., 1981). The overall reaction that occurs between 2.0–1.0 V is simply:

$$8\text{Li} + \text{Fe}_3\text{O}_4 \leftrightarrow 4\text{Li}_2\text{O} + 8\text{Fe} \quad (5)$$

During discharge, lithium is inserted into, and iron extruded from, a fixed cubic-close-packed (ccp) oxygen array that acts as the host framework for both lithium and iron (Thackeray et al., 1984b); intermediate ccp LiFe$_6$O$_8$, LiFeO$_2$, and Li$_2$FeO$_4$ phases are generated prior to the final Li$_2$O and Fe reaction products. The reaction is reversible; during charge, iron is reinserted and lithium is reoxidized prior to the final Li$_2$O and Fe reaction products. A major advantage of lithium-ion battery technology is that it is extremely versatile. The potential of the host electrodes and, therefore, the cell voltage can be tailored by the selection of (1) the structure type of the insertion electrode and (2) the electrochemically active redox centers. Consequently, lithium-ion cells can be designed with voltages between 1 and 5 V. By contrast, the voltage of most other battery systems is defined narrowly by their more specific cell chemistries, as in lead-acid, nickel–cadmium, nickel–metal hydride and sodium-nickel chloride batteries.

2. Required Properties of Li Insertion Electrodes

Lithium-ion cells operate by lithium insertion/extraction reactions that can be represented, in general, as:

$$\text{Li}_x\text{H}_a + \text{H}_c \leftrightarrow \text{H}_a + \text{Li}_x\text{H}_c \quad (6)$$

where H$_a$ and H$_c$ are the host anode and host cathode materials, such as graphite (C$_6$) and a transition metal oxide, respectively. Ideally, lithium insertion electrodes should have the following intrinsic properties:

- The host electrodes, H$_a$ and H$_c$, should accept and release as much lithium (x) as possible to provide a cell with high capacity and energy.
- The host electrodes should be stable over a wide compositional range (x) to ensure a good cycle life. In this respect, there should be minimal change to the unit cell parameters and volume of the host structures; the expansion/contraction of the unit cell should be isotropic rather than anisotropic.
- H$_a$ should have a low electrochemical potential vs. metallic lithium, whereas H$_c$ should have a high potential vs. lithium so that the cell has a high voltage.
- The structures of H$_a$ and H$_c$ should have an energetically-favorable interstitial space to allow fast Li$^+$ ion transport and they should be good electronic conductors to ensure high power.

The mineral world provides numerous examples of stable compounds that are produced under a variety of conditions, such as high temperature, high pressure, from solution and by ion-exchange. Mineral structures can, therefore, be used as a guide to identify and select stable insertion electrodes. It is perhaps not surprising that the three major cathode materials used in commercial lithium-ion cells have well known mineral structures, namely LiCoO$_2$ (rocksalt), LiMn$_2$O$_4$ (spinel) and LiFePO$_4$ (olivine) of which only LiFePO$_4$ is found in nature in its fully discharged state (triphylite) and in its fully delithiated state, FePO$_4$ (heterosite), although both triphylite and heterosite commonly contain Mn impurities. Synthetic LiFePO$_4$ electrodes are extremely stable to the repeated insertion and extraction of lithium.

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3. Cathode Materials

3.1 Limitations of existing electrode materials for lithium-ion systems

Schematic illustrations of the three commercially exploited lithium battery cathode structures, namely layered LiMO$_2$ (M = Co, Ni, Mn), spinel LiMn$_2$O$_4$ and olivine LiFePO$_4$ are shown in Figures 2(a)–(c), respectively. Despite their commercial use, the electrochemical properties of these electrodes are constrained in various ways by certain intrinsic limitations.

3.1.1 Layered LiMO$_2$ electrodes

When M = Co and/or Ni, the practical capacity of LiMO$_2$ electrodes is limited by the extent to which lithium can be inserted and, if reinserted into the Li$_{1-x}$MO$_2$ electrode structure. In practice, x is limited to ~0.5, which corresponds to an electrochemical capacity of ~140 mA·h/g (Mizushima et al., 1980). The delithiated structures are unstable at lower lithium content because of the high electrochemical potential (~4 V vs. Li$^0$) and high reactivity of the tetravalent Co$^{4+}$ and Ni$^{4+}$ ions, particularly with respect to the electrolyte. When M = Mn, the delithiated layered Li$_{1-x}$MnO$_2$ electrode is stabilized by a structural transformation to spinel, which lowers its average operating potential; the spinel-related electrode delivers most of its capacity below 3 V vs. Li$^0$.

3.1.2 Spinel LiMn$_2$O$_4$ electrodes

A Li$_{1-x}$MnO$_x$ spinel electrode delivers one-half of its capacity at ~4 V over the compositional range 0 ≤ x < 1 (Ohzuku et al., 2003). Although such spinel electrode delivers most of its capacity below 3 V vs. Li$^0$, the practical capacity of LiMO$_2$ electrodes is limited to ~0.5, which corresponds to an electrochemical capacity of ~140 mA·h/g (Mizushima et al., 1980).
et al., 1990; Thackeray et al., 1997), and the other half at ~3 V for 1 ≤ x ≤ 2 (Thackeray et al., 1983). Because there are two manganese ions per spinel formula unit, the 4-V capacity is restricted to 0.5 Li per transition metal ion, like the layered LiMO2 electrodes (M = Co, Ni) mentioned above in practical cells; the theoretical 4 V capacity of LiMn2O4 is 148 mA·h/g, most of which can be realized in practice. Discharge at 3 V is compromised by a severe crystallographic (Jahn-Teller) distortion as a result of the high concentration of Mn3+ in the electrode, which damages its cycling efficiency. Furthermore, LiMn2O4 spinel electrodes are prone to dissolution in the slightly acidic electrolytes of lithium-ion cells, which damages cycling stability, particularly at elevated temperature (~50°C). Nevertheless, despite these disadvantages, progress has been made to stabilize the spinel structure to counter these effects, notably by substituting a small amount of manganese in the spinel framework by lithium (Li1+Mn2–xO4), thereby raising the average oxidation state of the Mn ions above 3.5 (Gummow et al., 1994). The robust [Mn 2–δLiδ]O4 spinel framework with its three-dimensional interstitial space for lithium diffusion allows the spinel electrode to operate at extremely high rates.

3.1.3 Olivine LiFePO4 electrodes The olivine structure is the hexagonally-close-packed equivalent of the ccp spinel structure; both structure types can be represented in AB2O4 notation where A refers to cations in tetrahedral sites and B to cations in octahedral sites. Although all the lithium can be extracted from LiFePO4, i.e., 1 Li per transition metal ion (Fe), the theoretical capacity of the electrode (175 mA·h/g) is only slightly greater than that offered by LiMn2O4 (148 mA·h/g) because LiFePO4 also contains electrochemically inactive P cations (Padhi et al., 1997). The excellent stability of LiFePO4 to repeated lithium extraction and reinserterion and the ability to use stable nanosized particles, connected to one another by an electronically-conducting species such as carbon, helps to offset the intrinsically low ionic and electronic conductivity of LiFePO4 electrodes (Ravet et al., 2001). However, electrodes comprised of nano-sized particles tend to have a low packing (‘tap’) density which compromises the volumetric energy density of the cells.

The greatest limitation of all three cathode materials mentioned above is capacity. New approaches to design alternative materials are clearly required if lithium-ion batteries are to meet the demands of high-energy applications, such as plug-in hybrid vehicles, that will be dependent on batteries with sufficient energy and power to sustain the vehicle over longer distances than is currently possible.

3.2 Design of composite electrode structures Recent advances have been made in improving the capacity and stability of layered LiMO2 and spinel LiMn2O4 electrodes by integrating a structurally compatible component, such as Li2TiO3 (Kim et al., 2002) or Li2MnO3 (Johnson et al., 2005; Thackeray et al., 2005), into the close-packed parent structure. The approach follows the rationale of using two-component structures to design materials with significantly improved electrochemical properties. For example, in the family of solid electrolytes, it is well known that structures with anomalously high Ag+ ion conductivity at room temperature can be fabricated by reacting AgI with other iodide salts such as RbI and C11H30N3I3 to yield, respectively, RbAg4I5 (RbI·4AgI) (Hull et al., 2002) and Ag44I53(C11H30N3I3)3 (44AgI·3C11H30N3I3) (Thackeray et al., 1978). It is also now commonly known that Li2O units can stabilize a wide range of MnO2 electrode structures such as gamma-MnO2 and α-MnO2, resulting in Li2O·yMnO2 products with superior electrochemical properties compared to the parent MnO2 materials (Thackeray et al., 1993, 1997; Johnson et al., 1997).

Of particular significance are the advantages that Li2MnO3·LiMO2 (M = Mn, Ni, Co) composite electrode structures offer over conventional layered LiMO2 materials, such as LiCoO2, LiNiO2, LiMnO2, and combinations thereof (Thackeray et al., 2007). The structures are extremely complex; they are characterized by cation...
disorder between the highly integrated Li$_2$MnO$_3$- and LiMO$_2$ components. The Li$_2$MnO$_3$ component serves a vital role in stabilizing the LiMO$_2$ component and influencing the electrochemical properties of the electrode. For example, it is possible to activate the Li$_2$MnO$_3$ component by extracting Li$_2$O at high potentials, typically >4.5 V, to form a MnO$_2$ component within the charged electrode structure and, in so doing, to tailor and optimize compositional, structural and electrochemical properties (Johnson et al., 2004).

It is, however, important to maintain some unactivated Li$_2$MnO$_3$ in the composite Li$_2$MnO$_3$·LiMO$_2$ structure because it acts as a reservoir for excess lithium that can diffuse during the charging process from the transitional metal layers into adjacent lithium-depleted layers to stabilize the electrode structure (Grey et al., 2004). It is, however, important to maintain some unactivated Li$_2$MnO$_3$ in the composite Li$_2$MnO$_3$·LiMO$_2$ structure because it acts as a reservoir for excess lithium that can diffuse during the charging process from the transitional metal layers into adjacent lithium-depleted layers to stabilize the electrode structure (Grey et al., 2004).

The excellent electrochemical cycling behavior of a Li/0.3Li$_2$MnO$_3$·0.7LiMn$_{0.5}$Ni$_{0.5}$O$_2$ cell is shown in Figure 3, in which the typical voltage profile (40th cycle) is provided as an inset (Johnson et al., 2007). After the initial charge-discharge 'formation' cycle, the 0.3Li$_2$MnO$_3$·0.7LiMn$_{0.5}$Ni$_{0.5}$O$_2$ electrode provides an impressive, reversible capacity of approximately 230 mA·h/g between 4.8 and 2.75 V at a 0.25 mA/cm$^2$ rate, which is 64% greater than the typical practical capacity delivered by a standard LiCO$_2$ electrode (~140 mA·h/g).

Calorimetric studies have shown that Li$_2$MnO$_3$·LiMO$_2$ composite electrode structures generate less heat than conventional LiMO$_2$ electrodes (M = Co, Ni) when reacted with the electrolyte in their charged state; they exhibit a higher onset temperature, rendering them less prone to thermal runaway (Lu et al., 2006).

### 3.3 Cathodes for solid state lithium-polymer batteries

Despite the problems and safety limitations of using metallic lithium as an anode in lithium batteries, considerable success has been obtained in engineering all-solid-state Li/polymer electrolyte/metal oxide cells and batteries. The polyethyleneoxide-based solid polymer electrolyte suppresses lithium dendrite formation and the moss-like, high surface area- and highly reactive lithium that can be generated when liquid electrolyte lithium cells are cycled. Solid state lithium-polymer batteries are currently being manufactured for uninterrupted-power-supply (UPS) units; they are well suited for this purpose because UPS batteries are not often subjected to continuous charge/discharge cycling. The metal oxide cathode of choice for lithium-polymer cells is LiV$_3$O$_8$, the structure of which and that of its lithiated product, Li$_4$V$_3$O$_8$, are shown in Figure 4.

Both LiV$_3$O$_8$ and Li$_4$V$_3$O$_8$ have monoclinic symmetry, P2$_1$/m. The lattice constants of LiV$_3$O$_8$, namely, $a = 6.595$ Å; $b = 3.559$ Å; $c = 11.862$ Å; $\beta = 107.66^\circ$ change anisotropically on lithiation to Li$_4$V$_3$O$_8$, for which the corresponding parameters are $a = 5.955$ Å; $b = 3.911$ Å; $c = 11.915$ Å; $\beta = 107.03^\circ$ (de Picciotto et al., 1993a). Although $a$ and $b$ contract and expand markedly during the lithiation process, there is no significant change to the unit cell volume (265.36 and 265.33 Å$^3$, respectively). Despite the minimal change in unit cell volume, the anisotropic variation of the lattice parameters can cause severe cracking and loss of contact between electrode particles as illustrated by the image of lithiated Li$_4$V$_3$O$_8$ crystals obtained by reacting LiV$_3$O$_8$ with $n$-butyllithium at room temperature (Figure 5) (de Picciotto et al., 1993b).

Such damaging crystallographic phenomena must be countered by careful attention to binders and electronically conductive additives to ensure that electronic contact between the electrochemically-active electrode...
particles is maintained at all times during charge and discharge to guarantee an acceptable cycle life. The theoretical capacity of a LiV₃O₈ electrode for lithiation to Li₄V₃O₈ is 280 mA·h/g, almost all of which can be obtained in practice in lithium polymer cells at an average voltage of 2.5 V at slow current rates (West et al., 1996).

4. Anode Materials

4.1 Graphite

Graphite remains the anode material of choice for lithium-ion cells. Charged, lithiated graphite (LiC₆) electrodes operate at a potential just above that of metallic lithium (Dahn et al., 1995). Although the containment of lithium within the graphite sheets, and the protecting solid–electrolyte-interphase (SEI) layer that forms between the lithiated graphite particles and the electrolyte alleviate the problems of dendrite formation, there are still concerns about the high reactivity and safety of LiC₆ electrodes, particularly with respect to the flammable electrolyte solvents used in lithium-ion cells. For this reason, a concerted effort is being made by the international lithium battery community to find alternative anode materials that operate above the potential of lithiated graphite, such as lithiated metal oxides, metals, semimetals and intermetallic compounds.

4.2 Metal oxides

Metal oxide insertion electrodes are attractive alternatives to graphite because they react, in general, with lithium at potentials sufficiently far from the lithium potential. However, increasing the anode potential and improving the safety of a lithium-ion cell compromises the cell voltage, and hence the energy of the cell. For example, titanium oxide insertion electrodes such as Li₄Ti₅O₁₂ (Colbow et al., 1989), TiO₂ nanotubes and nanowires (Armstrong et al., 2004, 2006), and Li₂MTi₆O₁₄ (M = Ba, Sr) (Belharouak and Amine, 2003) that operate at approximately 1.5 V above the potential of metallic lithium, provide safe electrochemical couples when paired with LiCoO₂, LiMn₂O₄ and LiFePO₄ cathodes. The net voltage of these cells falls within the approximate range 2.5–2.0 V. The best known titanate anode is the spinel Li₄Ti₅O₁₂, that can be reformulated in spinel notation as Li[Li₁/₃Ti⁵/₃]O₄. Li₄Ti₅O₁₂ is an extremely stable compound; it can be prepared and used in nano-particulate form. The robust [Li₁/₃Ti⁵/₃]O₄ spinel framework, like the [Mn₂]O₄ spinel framework of Li[Mn₂]O₄, provides a three-dimensional space for rapid lithium-ion transport. A 2.5-V spinel–spinel couple comprising a Li₄Ti₅O₁₂ anode and lithium-stabilized Li¹⁺ₓMn₂⁻ₓO₄ couple was advocated several years ago as a safe electrochemical couple (Ferg et al., 1994). During charge and discharge, lithium is simply transferred between two cubic host spinel structures (Figure 6); during these reactions, there is essentially no volume expansion or contraction of the [Li₁/₃Ti⁵/₃]O₄ spinel framework, whereas the [Li,Mn₂⁺]O₄ framework expands and contracts isotropically by only ~5%. High-rate Li₄Ti₅O₁₂–Li¹⁺ₓMn₂⁻ₓO₄ lithium-ion batteries are currently receiving considerable interest for hybrid electric vehicles, in which the battery is used predominantly as a ‘power assist’ to improve the fuel efficiency of the vehicle.

Fairly recently, nanoparticulate metal oxides such as CoO that operate by reversible lithium insertion-metal displacement reactions were suggested as possible alternative anode materials (Poizot et al., 2000):

\[ 2\text{Li} + \text{CoO} \leftrightarrow \text{Li}_2\text{O} + \text{Co} \] (7)
These reactions are not fully reversible and are often characterized by severe hysteresis at high potentials that compromises their use in practical cells. However, such reactions warrant further investigation because it has already been demonstrated that they can be highly reversible, as in high-temperature Na/NiCl₂ (Sudworth, 2001) and Li/Fe₃O₄ (Thackeray et al., 1981, 1984b) cells in which the anion lattice provides a stable framework for the cations during discharge and charge. In particular, the reaction of the Na/NiCl₂, ‘Zebra’ battery:

\[ 2\text{Na} + \text{NiCl}_2 \leftrightarrow 2\text{NaCl} + \text{Ni} \]  

(8)

that produces common salt (NaCl) and extruded Ni on discharge, is 100% coulombically efficient. The outstanding efficiency of this electrochemical reaction can be attributed to the excellent electronic contact that is maintained between the finely divided NiCl₂, NaCl and Ni particles within the cathode matrix at all times during discharge and charge.

4.3 Metals, semimetals and intermetallic compounds

Several metals, such as aluminium and tin, and semimetals such as silicon are attractive anode materials for lithium batteries because they can accommodate a significant quantity of lithium within their structures at potentials less than 1 V vs. Li⁰. However, because metals and semimetals have dense, compact structures, lithium insertion is often accompanied by large volumetric changes and by structural transformations. For example, lithium insertion into aluminium necessitates a major structural rearrangement of the Al atoms during the transition from the face-centered-cubic (fcc) lattice of the parent compound to the fcc lattice of the LiAl product, as shown in Figure 7; the transition results in an increase in the unit cell volume of approximately 100% (per Al atom). Such severe crystallographic changes result in a break-up of the electrode particles, loss of electronic contact between particles and cycling inefficiency. Significant progress has been made to alleviate these problems by using sputtered thin-film electrodes, notably those containing silicon, and by aligning the deposited electrode matrix so that the volumetric expansion can be accommodated in void spaces between them. However, such techniques are expensive compared to conventional powdered electrode processing techniques.

It is perhaps not surprising that it was Sony Corp., the pioneers and originators of commercial Li₃C₆/ LiCoO₂ lithium-ion batteries, who were also first to introduce lithium-ion cells with intermetallic anodes into the battery market (Ogisu, 2005). Sony’s ‘Nexelion’ cells, as they are commonly referred to, contain an amorphous Co–Sn–C anode and a lithium-manganese–nickel–cobalt-oxide cathode. During charge and discharge, lithium is cycled in and out of a Li,Sn alloy that is embedded within an inactive Co–C matrix, following principles described by Mao et al., (1999). Although it has been reported that Nexelion cells can provide 30% higher capacity than conventional lithium-ion cells, they are targeted for niche applications, such as camcorders. Nevertheless, despite their limited application at present, the introduction of intermetallic anodes in commercial cells bodes well for continued improvements and further exploitation of lithium-ion battery technology.

Over the past few years, several intermetallic compounds have been identified that operate by lithium insertion-metal displacement reactions. In an attempt to find materials that might offer good electrochemical reversibility, an approach has been adopted to seek for systems in which there is a strong structural relationship between the parent compound and its lithiated products. An excellent example is InSb, which has a fcc zinc-blende, diamond-like lattice (Vaughhey et al., 2000). Lithium insertion into InSb, which occurs just below 1 V vs. Li⁰, is accompanied by the extrusion of Sb array, which remains intact throughout the electrochemical reaction, expands by a mere 4%. When the extruded In is taken into consideration, the electrode expands overall by 46.5%. This room temperature reaction, which is analogous to the high-temperature Na/NiCl₂ reaction of ‘Zebra’ cells, is reversible. However, capacity is lost on cycling Li/InSb cells, which is attributed to an exaggerated grain growth of the extruded In crystallites (whiskers) and the loss of electronic contact between the In and Li,Sb particles. In principle, however, with an improved electrode design and the suppression of In crystal growth, it should be possible to increase the cycling efficiency and cycling stability of the InSb electrode. Although InSb is an excellent semiconductor and has the structural properties that make it an excellent candidate for further exploitation, its prohibitive cost and the toxicity of Sb-containing compounds preclude its use in practical lithium-ion cells.

By comparison, the intermetallic compound, Cu₃Sn₈ (Kepler et al., 1999) is more attractive as an anode material because 1) it operates below 0.5 V vs.
Li\(^0\), 2) it is relatively inexpensive, and 3) Cu is the current collector of choice in the anode electrode of conventional lithium-ion batteries. Cu\(_6\)Sn\(_5\) has a NiAs-type structure that transforms topotactically on lithiation to a lithiated zinc-blende-type structure, Li\(_2\)CuSn, as shown schematically in Figure 8.

The ideal transformation of the CuSn (‘NiAs-type’) framework in Cu\(_6\)Sn\(_5\) to the CuSn (‘zinc-blende’) framework of Li\(_2\)CuSn is accomplished by 1) the introduction of 10 Li atoms, 2) the internal displacement of 50\% of the Sn atoms into interstitial sites, and 3) the extrusion of 1 Cu atom per Cu\(_6\)Sn\(_5\) formula unit (Kepler et al., 1999; Thackeray et al., 2003). Despite the relatively large crystallographic volume change during the NiAs to lithiated zinc-blende transition (59\%), the process is reversible, although it occurs with some hysteresis. Further lithiation of Li\(_2\)CuSn displaces more copper from the structure to yield, first, a Li\(_{2x}\)Cu\(_{1–x}\)Sn solid solution within the range 0 < x < 1 and then a binary Li\(_x\)Sn product with x\(_{\text{max}}\) = 4. Highly lithiated Cu\(_6\)Sn\(_5\) electrodes cycle with lower efficiency than those cycled to an end composition Li\(_2\)CuSn (Kepler et al., 1999); it has recently been demonstrated that substituted Cu\(_{6–x}\)M\(_x\)Sn\(_5\) electrodes (M = Co, Ni, Zn, x = 1) provide a superior capacity to Cu\(_6\)Sn\(_5\) (Vaughhey et al., 2007). Such lithium insertion/metal extrusion reactions hold promise for further exploitation, particularly if nanosized intermetallic particles can be used to improve the rate capability of intermetallic electrodes and if the problems associated with volumetric expansion and the maintenance of electronic conductivity during electrochemical cycling can be overcome.

Conclusions

The versatility of lithium-ion battery chemistry and the possibility of designing new electrode and electrolyte materials or improving existing ones will ensure that lithium battery research and development will continue for many more years to come. Paramout to the future success of high energy lithium-ion batteries will rest in the ability to control the chemical and electrochemical reactivity of high capacity electrode materials, particularly those that operate at high or low potentials vs. metallic lithium.

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Fig. 8 The topotactic transformation of Cu\(_6\)Sn\(_5\) (nickel-arsenide-type structure) to Li\(_2\)CuSn (lithiated zinc-blende-type structure)


