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 LiCoO_2 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 CO_2 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 $\text{Li}_x\text{C}_6/\text{Li}_{1-x}\text{CoO}_2$ 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 $\text{Li}_{1-x}\text{CoO}_2$ 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 $\text{Li}_x\text{C}_6/\text{Li}_{1-x}\text{CoO}_2$ 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 LiMn_2O_4 (Thackeray *et al.*, 1984a; Ohzuku *et al.*, 1990) and its substituted derivatives (Gummow *et al.*, 1994), and LiFePO_4 (olivine)

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Table 1 Selected battery systems and their theoretical electrochemical properties (based on the masses of active electrode and electrolyte components only)

System	Negative electrode	Positive electrode	OCV (V)	Th. Cap (Ah/kg)	Th En. (Wh/kg)
Lead – acid	Pb	PbO ₂	2.1	83	171
Ni-Cd	Cd	NiOOH	1.35	162	219
Ni-MH	MH alloy	NiOOH	1.35	~178	~240
Na-S (350°C)	Na	S	2.1-1.78 (2.0)	377	~754
Na-MCl ₂ (300°C)	Na	NiCl ₂	2.58	305	787
Li-Ion	Li _x C ₆	Li _{1-x} CoO ₂	4.2-3.0 (~3.8)	158 (x=1.0)	~600
Li-polymer	Li	Li _{1+x} V ₃ O ₈	~3.3-2.0 (~2.6)	~340 (x=4)	~884
Li-S	Li	S	>2	1169	>2338

Fig. 1 Energy density plots of various batteries

(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 Li_{1+x}M_{1-x}O₂ 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 Li_{1-x}CoO₂ cathodes, according to reactions (1) and (2), respectively (Linden and Reddy, 2002):

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 Li_{1-x}CoO₂ (0 ≤ x ≤ 1) electrodes. For delithiated Li_{1-x}CoO₂ electrodes, however, x_{max} is limited in practice to approximately 0.5 because the structure becomes unstable at higher values of x.

Reversible displacement reactions, sometimes referred to as ‘conversion’ reactions, in which new phases are constructed during discharge and charge, can occur by multi-electron transfer processes, as exemplified by the reactions of lead-acid- and high-temperature sodium–nickel chloride batteries that allow for the transfer of 2 electrons per Pb and Ni redox centers, respectively, as shown in reactions (3) and (4) (Sudworth, 2001; Linden and Reddy, 2002):

High-temperature Li/iron-oxide (Fe_3O_4 , spinel) cells operate by combined lithium insertion/metal displacement reaction processes in the cathode that involve 2.33 electrons per iron atom (Thackeray *et al.*, 1981). The overall reaction that occurs between 2.0–1.0 V, is simply:

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_5O_8 , LiFeO_2 and Li_5FeO_4 phases are generated prior to the final Li_2O and Fe reaction products. The reaction is reversible; during charge, iron is re-accommodated within the ccp oxygen array and lithium is deposited at the anode. A similar lithium insertion/copper displacement reaction has been reported for $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$ (Morcrette *et al.*, 2003). Although such lithium insertion/metal displacement reactions occur at lower potentials than lithium insertion/extraction reactions with LiCoO_2 , LiMn_2O_4 and LiFePO_4 , they offer, in principle, the possibility of increasing the cathode capacity and hence the energy delivered by lithium cells and batteries.

2. Required Properties of Li Insertion Electrodes

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

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_2O_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.

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.

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 ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}$), spinel LiMn_2O_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 $\text{M} = \text{Co}$ and/or Ni , the practical capacity of LiMO_2 electrodes is limited by the extent to which lithium can be extracted from, and reinserted into the $\text{Li}_{1-x}\text{MO}_2$ electrode structure. In practice, x is limited to ~ 0.5 , which corresponds to an electrochemical capacity of $\sim 140 \text{ mA}\cdot\text{h/g}$ (Mizushima *et al.*, 1980). The delithiated structures are unstable at lower lithium content because of the high electrochemical potential ($\sim 4 \text{ V vs. Li}^0$) and high reactivity of the tetravalent Co^{4+} and Ni^{4+} ions, particularly with respect to the electrolyte. When $\text{M} = \text{Mn}$, the delithiated layered $\text{Li}_{1-x}\text{MnO}_2$ 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_2O_4 electrodes A $\text{Li}_x\text{Mn}_2\text{O}_4$ spinel electrode delivers one-half of its capacity at $\sim 4 \text{ V}$ over the compositional range $0 \leq x < 1$ (Ohzuku

Fig. 2 Schematic illustrations of the structures of (a) LiMO_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}$); (b) LiMn_2O_4 ; (c) LiFePO_4 . Lithium ions are shown as dots; the remaining cations reside within shaded O polyhedra

et al., 1990; Thackeray *et al.*, 1997), and the other half at ~ 3 V for $1 \leq x \leq 2$ (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 LiMO_2 electrodes ($\text{M} = \text{Co}, \text{Ni}$) mentioned above in practical cells; the theoretical 4 V capacity of LiMn_2O_4 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 Mn^{3+} in the electrode, which damages its cycling efficiency. Furthermore, LiMn_2O_4 spinel electrodes are prone to dissolution in the slightly acidic electrolytes of lithium-ion cells, which damages cycling stability, particularly at elevated temperature ($\sim 50^\circ\text{C}$). 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 ($\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$), thereby raising the average oxidation state of the Mn ions above 3.5 (Gummow *et al.*, 1994). The robust $[\text{Mn}_{2-\delta}\text{Li}_\delta]\text{O}_4$ 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 LiFePO_4 electrodes The olivine structure is the hexagonally-close-packed equivalent of the ccp spinel structure; both structure types can be represented in AB_2O_4 notation where A refers to cations in tetrahedral sites and B to cations in octahedral sites. Although all the lithium can be extracted from LiFePO_4 , 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 LiMn_2O_4 (148 mA·h/g) because LiFePO_4 also contains electrochemically inactive P cations (Padhi *et al.*, 1997). The excellent stability of LiFePO_4 to repeated lithium extraction and reinsertion 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 LiFePO_4 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 LiMO_2 and spinel LiM_2O_4 electrodes by integrating a structurally compatible component, such as Li_2TiO_3 (Kim *et al.*, 2002) or Li_2MnO_3 (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 $\text{C}_{11}\text{H}_{30}\text{N}_3\text{I}_3$ to yield, respectively, RbAg_4I_5 ($\text{RbI} \cdot 4\text{AgI}$) (Hull *et al.*, 2002) and $\text{Ag}_{44}\text{I}_{53}(\text{C}_{11}\text{H}_{30}\text{N}_3\text{I}_3)_3$ ($44\text{AgI} \cdot 3\text{C}_{11}\text{H}_{30}\text{N}_3\text{I}_3$) (Thackeray *et al.*, 1978). It is also now commonly known that Li_2O units can stabilize a wide range of MnO_2 electrode structures such as $\gamma\text{-MnO}_2$ and $\alpha\text{-MnO}_2$, resulting in $\text{Li}_2\text{O} \cdot y\text{MnO}_2$ products with superior electrochemical properties compared to the parent MnO_2 materials (Thackeray *et al.*, 1993, 1997; Johnson *et al.*, 1997).

Of particular significance are the advantages that $\text{Li}_2\text{MnO}_3 \cdot \text{LiMO}_2$ ($\text{M} = \text{Mn}, \text{Ni}, \text{Co}$) composite electrode structures offer over conventional layered LiMO_2 materials, such as LiCoO_2 , LiNiO_2 , LiMnO_2 , and combinations thereof (Thackeray *et al.*, 2007). The structures are extremely complex; they are characterized by cation

Fig. 3 Electrochemical cycling behavior of a lithium cell with a $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ composite cathode structure between 4.8 and 2.75 V at 50°C . Figure reproduced from Johnson *et al.* (2007) with permission from Elsevier

disorder between the highly integrated Li_2MnO_3 - and LiMO_2 components. The Li_2MnO_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_2MnO_3 component by extracting Li_2O 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_2MnO_3 in the composite $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ 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), thereby allowing high practical capacities (>200 mA·h/g) to be delivered reversibly on charge and discharge. Moreover, the Li_2MnO_3 component serves not only as a stabilizing agent, but it also contributes as an electrolyte to facilitate Li^+ -ion transport between the electrochemically active regions of the electrode structure.

The excellent electrochemical cycling behavior of a $\text{Li}/0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ 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 $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode provides an impressive, reversible capacity of approximately 230 mA·h/g between 4.8 and 2.75 V at a 0.25 mA/cm² 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 $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ composite electrode structures gen-

Fig. 4 The anisotropic crystallographic transformation of LiV_3O_8 to $\text{Li}_4\text{V}_3\text{O}_8$ that occurs without volume change

erate less heat than conventional LiMO_2 electrodes ($\text{M} = \text{Co}, \text{Ni}$) 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 $\text{Li}/\text{polymer electrolyte}/\text{metal oxide}$ 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_3O_8 , the structure of which and that of its lithiated product, $\text{Li}_4\text{V}_3\text{O}_8$, are shown in **Figure 4**.

Both LiV_3O_8 and $\text{Li}_4\text{V}_3\text{O}_8$ have monoclinic symmetry, $\text{P2}_1/\text{m}$. The lattice constants of LiV_3O_8 , namely, $a = 6.595$ Å; $b = 3.559$ Å; $c = 11.862$ Å, $\beta = 107.66^\circ$ change anisotropically on lithiation to $\text{Li}_4\text{V}_3\text{O}_8$, 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 Å³, 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 $\text{Li}_4\text{V}_3\text{O}_8$ crystals obtained by reacting LiV_3O_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

Fig. 6 Schematic illustration of a $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ 'spinel-spinel' lithium-ion cell

Fig. 5 LiV_3O_8 crystals (a) before and (b) after lithiation with *n*-butyllithium at room temperature

particles is maintained at all times during charge and discharge to guarantee an acceptable cycle life. The theoretical capacity of a LiV_3O_8 electrode for lithiation to $\text{Li}_4\text{V}_3\text{O}_8$ 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 (LiC_6) 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 LiC_6 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 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Colbow *et al.*, 1989), TiO_2 nanotubes and nanowires (Armstrong *et al.*, 2004, 2006), and $\text{Li}_2\text{MTi}_6\text{O}_{14}$ (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 LiCoO_2 , LiMn_2O_4 and LiFePO_4 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 $\text{Li}_4\text{Ti}_5\text{O}_{12}$, that can be reformulated in spinel notation as $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is an extremely stable compound; it can be prepared and used in nano-particulate form. The robust $[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ spinel framework, like the $[\text{Mn}_2]\text{O}_4$ spinel framework of $\text{Li}[\text{Mn}_2]\text{O}_4$, provides a three-dimensional space for rapid lithium-ion transport. A 2.5-V spinel-spinel couple comprising a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode and lithium-stabilized $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ 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 $[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ spinel framework, whereas the $[\text{Li}_x\text{Mn}_{2-x}]\text{O}_4$ framework expands and contracts isotropically by only ~5%. High-rate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ 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):

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:

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 Li_xC₆/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_xSn alloy that is embedded within an inactive Co-C

Fig. 7 The fcc-fcc transition of Al to LiAl

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 (Vaughey *et al.*, 2000). Lithium insertion into InSb, which occurs just below 1 V vs. Li⁰, is accompanied by the extrusion of In metal to yield Li₃Sb (Tostmann *et al.*, 2002); the fcc 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 Li₃Sb 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, Cu₆Sn₅ (Kepler *et al.*, 1999) is more attractive as an anode material because 1) it operates below 0.5 V vs.

Fig. 8 The topotactic transformation of Cu_6Sn_5 (nickel-arsenide-type structure) to Li_2CuSn (lithiated zinc-blende-type structure)

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_6Sn_5 has a NiAs-type structure that transforms topotactically on lithiation to a lithiated zinc-blende-type structure, Li_2CuSn , as shown schematically in **Figure 8**.

The ideal transformation of the CuSn ('NiAs-type') framework in Cu_6Sn_5 to the CuSn ('zinc-blende') framework of Li_2CuSn 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_6Sn_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_2CuSn displaces more copper from the structure to yield, first, a $\text{Li}_{2+x}\text{Cu}_{1-x}\text{Sn}$ solid solution within the range $0 < x < 1$ and then a binary Li_xSn product with $x_{\text{max}} \approx 4$. Highly lithiated Cu_6Sn_5 electrodes cycle with lower efficiency than those cycled to an end composition Li_2CuSn (Kepler *et al.*, 1999); it has recently been demonstrated that substituted $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$ electrodes ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}$, $x = 1$) provide a superior capacity to Cu_6Sn_5 (Vaughey *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. Paramount 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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