Conf-950259--1

SAND 94-2763C

RECENT ADVANCES IN LITHIUM ION TECHNOLOGY

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This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

Introduction

Lithium ion technology is based on the use of lithium intercalating electrodes. Carbon is the most commonly used anode material, while the cathode materials of choice have been layered lithium metal chalcogenides ($LiMX_2$) and lithium spinel-type compounds. Electrolytes may be either organic liquids or polymers. Although the first practical use of graphite intercalation compounds as battery anodes was reported in 1981 for molten salt cells (1) and in 1983 for ambient temperature systems (2), it was not until Sony Energytech announced a new lithium ion rechargeable cell containing a lithium ion intercalating carbon anode in 1990, that interest peaked. The reason for this heightened interest is that these cells have the high energy density, high voltage and light weight of metallic lithium systems plus a very long cycle life, but without the disadvantages of dendrite formation on charge and the safety considerations associated with metallic lithium.

Carbon Anodes

Lithium ions intercalate into ordered carbons in staged phases. The crystallinity and microstructure, i.e., ordering, vary with the starting material, the preparation method, and heat treatment. Carbons made at low temperatures (< 1000° C) have a disordered structure. Increasing the temperature increases the amount of crystallinity until the structure becomes highly ordered at > 2200°C, where it approaches the graphite structure. A high degree of crystallinity promotes a higher degree of intercalation, while defects, structural imperfections, and disorder generally hinder intercalation. Small crystallite size and random stacking of adjacent layers are associated with disorder.

The crystal structure of the most common form of graphite consists of planar sheets of carbon in a hexagonal pattern that are stacked in registered fashion in the sequence ABABAB..., known as hexagonal or 2H graphite. Every other layer is aligned, while alternate layers are offset (Figure 1). Upon intercalation of lithium into the graphitic structure, the carbon layers shift to AAAA... stacking, i.e., all the layers become aligned (Figure 2). This occurs because the lowest energy state for the intercalated lithium ion occurs when it is nested symmetrically between two hexagonal carbon arrays. The lithium ions enter the graphite matrix in stages, the stage number corresponding to the number of graphitic layers separating two intercalated layers. The theoretical limit occurs at LiC_6, in which lithium ions fill every layer (stage 1). In disordered carbons, e.g., petroleum coke, lithium ions can intercalate to $Li_{0.5}C_6$. The intercalation is not staged because the

lithium resides in low energy sites which are spatially separated.

In a practical cell, some fraction of the charge passed during lithium intercalation into the carbon anode will be irreversibly lost on the first discharge. This loss is due mainly to the formation of a passivating layer, commonly referred to as the solid electrolyte interface (SEI), on the surface of the carbon through the irreversible consumption of electrons and electrolyte solvent. This process is a function of electrolyte solvent because the lithium ions are solvated and the solvent molecules tend to cointercalate with the lithium. Insertion of this large aggregate into the carbon structure causes exfoliation and the generation of more surface area which then becomes passivated. The use of certain cosolvents or complexing agents can reduce this effect by either minimizing the amount of solvent cointercalation or stabilization of the SEI (3, 4).

Low temperature carbons, e.g., coke, exhibit a relatively small irreversible loss of lithium. This is due to the large percentage of unorganized structure which limits lattice expansion, minimizing solvent cointercalation. However, the reversible capacity is low , and a sloped discharge is obtained, consistent with the variation in site energies in the disordered matrix. Conversely, high temperature carbons, e.g., graphite, yield high reversible capacity with a flat discharge curve, since all of the lithium sites are identical with equivalent binding energies (5).

Some disordered carbons have been synthesized recently having a specific capacity greater than that expected from LiC_6, (e.g., reference 6), suggesting that a different mechanism of lithium storage is occurring. One theory, based on NMR studies, states that there are two forms of lithium in the charged carbon (7). The first is ionic, similar to that found in graphite, and the second is molecular or covalent Li_2 located in the defective portion of the lattice. On discharge, the ionic lithium is deintercalated first, and the Li_2 molecules act as a reservoir, filling the sites vacated by the ionic lithium on discharge. A second theory defines two regions in the carbon; layers and cavities (8). On charge, lithium ions intercalate into the layers and are doped into the cavities simultaneously. On discharge, lithium ions will deintercalate from the layers first, and then be dedoped from the cavities through the interlayers.

Cathode Materials

Layered lithium chalcogenides of the formula $LiMX_2$ and lithium spinel-type compounds are the most commonly studied materials as insertion cathodes for use with lithium intercalated carbon anodes. Of these, the layered materials $LiCoO_2$ and $LiNiO_2$ and the three dimensional spinel $LiMn_2O_4$ are the only ones capable of reversibly intercalating lithium ions at > 3.5 V (9). $LiTiS_2$ has been investigated as a cathode for lower voltage (~2 V) systems (10).

Lithium Cobalt Oxide. $LiCoO_2$ has a layered, rock salt structure with lithium and cobalt cations occupying alternate layers of octahedral sites in a distorted cubic close packed oxygen ion lattice. The layered CoO_2 framework provides a two-dimensional interstitial space allowing lithium ions to be easily removed. In the reversible reaction:

$$6C + LiCoO_2 \Leftrightarrow Li_xC_6 + Li_{1-x}CoO_2$$

x can vary between $0 \le x \le 0.9$. However, in practical cells, the instability of Co^{+4} causes the process to be limited to the range $0 \le x \le 0.5$, resulting in a practical specific capacity of 137 mAh/g, with an average discharge voltage of 3.9 V (11).

Lithium Nickel Oxide. $LiNiO_2$ has a similar structure to that of $LiCoO_2$ described above. Similarly, in the reversible reaction:

$$6C + LiNiO_2 \Leftrightarrow Li_xC_6 + Li_{1-x}NiO_2$$

the reactivity of Ni^{+4} limits the value of x to $0 \leq x \leq 0.5$, giving a practical specific capacity of 137 mAh/g. The C/$LiNiO_2$ system has an average discharge voltage of 3.5 V (11).

Lithium Manganese Oxide. Lithium ions can be inserted into the three dimensional $LiMn_2O_4$ spinel structure. Upon insertion, they diffuse through a network of face-sharing tetrahedra and octahedra with a corresponding reduction of the manganese ions. The lithium can be reversibly removed from $LiMn_2O_4$ to form λ-MnO_2 at a potential of 4 V vs. Li, or a second lithium can be reversibly inserted at 2.9 V (12). The cell reaction for the 4 V plateau is:

$$6C + LiMn_2O_4 \Leftrightarrow Li_xC_6 + Li_{1-x}Mn_2O_4$$

with x limited to $0 \leq x \leq 0.73$. This leads to a practical specific capacity of 120 mAh/g. The system has an average discharge voltage of 3.9 V. Some work is also in progress looking at defect spinels with the general formula $Li_2O \cdot yMnO_2$ as cathode materials (13).

Lithium Titanium Disulfide. The TiS_2 structure consists of Ti atoms octahedrally surrounded by two layers of S atoms in a hexagonally close-packed arrangement. The S-Ti-S sandwiches are stacked, and lithium ions can diffuse into the two-dimensional gaps between the layers where they occupy octahedral sites. One advantage of TiS_2 is its good electrical conductivity, in both the charged and discharged states, eliminating the need for a conductive additive when fabricating composite electrodes. The reversible cell reaction can be written as:

$$6C + LiTiS_2 \Leftrightarrow Li_xC_6 + Li_{1-x}TiS_2$$

Over the range of $0 \leq x \leq 1$, the average discharge voltage is 2.1 V and the practical specific capacity is ~ 200 mAh/g.

Electrolytes

Both liquid and polymeric electrolytes have been used with lithium ion systems. Liquid electrolytes frequently consist of binary mixtures of solvents. To maximize the conductivity, one solvent generally has a high dielectric constant and the second a low viscosity. A number of lithium salts are stable and soluble in these solvent mixtures, but all have disadvantages, e.g., low conductivity, toxicity, safety, corrosion of grids, etc. Work is continuing to find suitable solute-solvent combinations for the various combinations of anode and cathode materials selections.

The electrolyte plays an important role in the intercalation reactions at the carbon anode. For example, some solvents, e.g., propylene carbonate, are cointercalated with lithium and cause exfoliation of the carbon matrix, resulting in higher passivation and shorter cycle life. Others decompose on the carbon surface. Solid polymer electrolytes are being developed to eliminate the reactivity issues of the liquid electrolytes. The main difficulty associated with the polymer electrolytes is poor room temperature conductivity. To overcome this difficulty, solvents are added to the polymer network to form a gel system (14). These systems are dimensionally stable and have conductivities approaching those of liquid organic electrolytes.

State of the Art

Although much research is ongoing worldwide, only a few companies are producing lithium ion batteries. Most of the production is specifically designed for electronic devices, e.g., cellular telephones, camcorders, laptop computers, etc., therefore little performance data is available. Companies currently manufacturing lithium ion batteries for sale include: A&T Battery Co., Matsushita, Sanyo, Sony and others, all located in Japan. Production cells are capable of delivering 400 mAh in the AA size at the 0.2 C rate at room temperature, dropping slightly with increased rate (~ 18% for a 10x increase in rate). Energy density is quoted at 78 Wh/kg and 192 Wh/l, increasing as the cell size increases. A cycle life of 1200 cycles to 100% depth of discharge is advertised. Self discharge has been measured at 12% the first month, 21% after 3 months and 30% after 6 months at room temperature storage (15).

Sandia Programs

Battery Technology Initiative. This program is a Cooperative Research and Development Agreement (CRADA) between Sandia and four industrial partners; AT&T Bell Labs., Eveready Battery Co., Rayovac Corp. and Wilson Greatbatch Ltd. The goal of this program is to develop a carbon, based on prior Sandia technology, that is suitable as an anode in lithium ion rechargeable cells. Certain carbon foams, developed for military applications, have been shown to intercalate lithium ions very efficiently. Processing variables are being studied in a controlled fashion, and the resulting carbonaceous materials are then physically characterized. Electrochemical screening is carried out on the samples, i.e., intercalation efficiency and irreversible passivation; materials that pass the test are sent to the industrial partners for evaluation in their electrode configurations. Thus, the research and development steps are performed in parallel, shortening the time to commercialization. Results to date have been encouraging, with some carbon samples achieving a reversible capacity of ~600 mAh/g. However, the irreversible passivation is high. Work is now focusing on reducing the passivation, while maintaining the high reversible capacity.

Flexible Carbon Anode. This is a Sandia funded program (Laboratory Directed Research and Development) to develop a thin, flexible carbon anode for use in lithium ion rechargeable cells. In typical cells, the anode is formed from a powdered carbon that is mixed with an inert binder, e.g., Teflon, to obtain a flexible electrode. The presence of a binder reduces the amount of carbon in the electrode, resulting in a lower capacity and energy. Under certain circumstances, the binder might block some active sites on the carbon, further lowering the capacity and energy, or it might hinder the movement of lithium ions into and out of the carbon, limiting its rate capability.

To minimize these effects, we have developed a thin, flexible carbon fiber that intercalates lithium ions to the same level as many powdered carbons. This fiber can be woven, knitted or matted into a cloth for use as an anode in lithium ion rechargeable cells. The absence of binder and current collector should maximize the capacity and energy density of these cells. The flexible carbon materials were prepared from a commercial poly(acrylonitrile) (PAN) fiber by preoxidizing in air at temperatures ranging from 230° to 290° C and then pyrolyzing in argon over the temperature range of 900° to 1400° C. Electrochemical tests indicated certain of these fibers capable of delivering a reversible capacity in excess of 450 mAh/g. Carbon cloths prepared from PAN filaments under the same conditions as above are also being tested. Capacities in excess of 300 mAh/g have been obtained in preliminary tests. Passivation was quite low, on the order of 50 mAh/g. Work is continuing to improve the capacity and demonstrate feasibility in a spirally wound cell.

Lithium Manganese Oxide Doping. The purpose of this DOE/Basic Energy Sciences (BES) funded program is to understand the influence that doping of lithium manganese oxide has on the fundamental properties that control its performance as a cathode. While the effects of surface area, pore volume and grain size can be manipulated in several ways, only doping the crystalline material can change the bulk properties of a given phase of $Li_xMn_2O_4$. The program consists of three phases: solid state molecular modeling of doped $Li_xMn_2O_4$, synthesis of materials based on predictions of the model, and electrochemical evaluation of the newly synthesized materials.

Substitutional and interstitial doping of various metals to adjust the crystal lattice and spinel framework of $Li_xMn_2O_4$ will modify the diffusion of ions and the ability of the lattice to accomodate the expansion and contraction that occurs during lithiation. We have successfully modeled the insertion and deinsertion of lithium into the spinel phase of undoped $Li_xMn_2O_4$, and are now comparing the effect of the addition of dopants on the lattice energy and lattice parameters. In addition, we have demonstrated proof-of-concept for a new nonaqueous precipitation method for preparing lithiated manganese oxides.

Electric Vehicle Research and Development. Sandia National Laboratories is participating in a CRADA with the US Advanced Battery Consortium (USABC) to develop lithium ion battery technology for Electric Vehicles (EVs). The tasks include materials development for lithium polymer batteries. Sandia also provides technical support for tasks that range from modeling cells and cell components (e.g. electrode shape effects on cell performance), recycling and reclamation studies on rechargeable batteries and preparing a safety test plan. Finally, Sandia provides testing and performance evaluation for our research and development projects as well as for other USABC contractors. This testing is performed with complete confidentiality and is reported to USABC and its contractors.

Reporting on these activities is outside the scope of this paper but can be obtained from other sources (16).

Summary

The lithium ion battery, based on the intercalation/deintercalation of lithium ions into host electrodes, is a promising new technology for powering portable electronic devices. Several chemistries are being considered for commercial products, and a few companies are selling these batteries in specific configurations. The 4 volt AA cells presently on the market have an energy density of 78 Wh/kg, with somewhat higher values obtainable in larger cells.

Sandia National Laboratories has four programs in the area of lithium ion technology. All are concerned with improving materials properties. The first, a cooperative research and development agreement with four companies, is focused on developing carbon intercalation anodes having high capacity and low passivation. The second, an internally funded program, is looking at flexible carbon materials as anodes in lithium ion cells. This type of anode will eliminate the need for an inert binder, resulting in higher energy and improved rate capability. The third program, funded by

DOE/BES, is concerned with developing an improved lithiated manganese spinel cathode by doping the backbone structure with foreign ions. The program consists of three phases; molecular modeling, synthesis of doped materials, and electrochemical testing. The fourth, a CRADA with the USABC, includes materials development for a lithium ion polymer electrolyte battery, as well as modeling, recycling and safety studies. All programs are fairly recent and work is in progress. Initial results in all four are promising.

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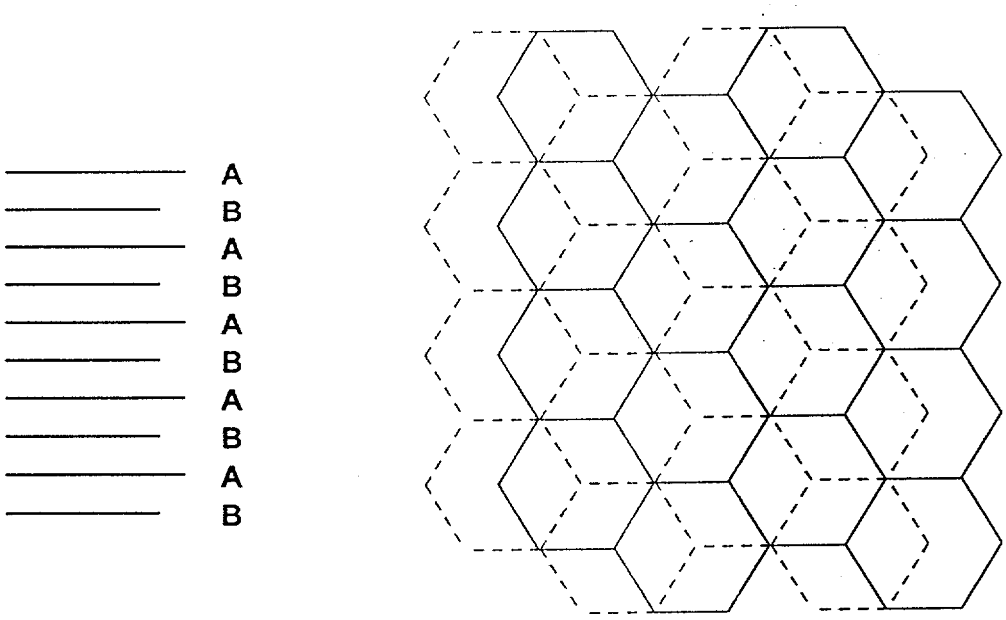
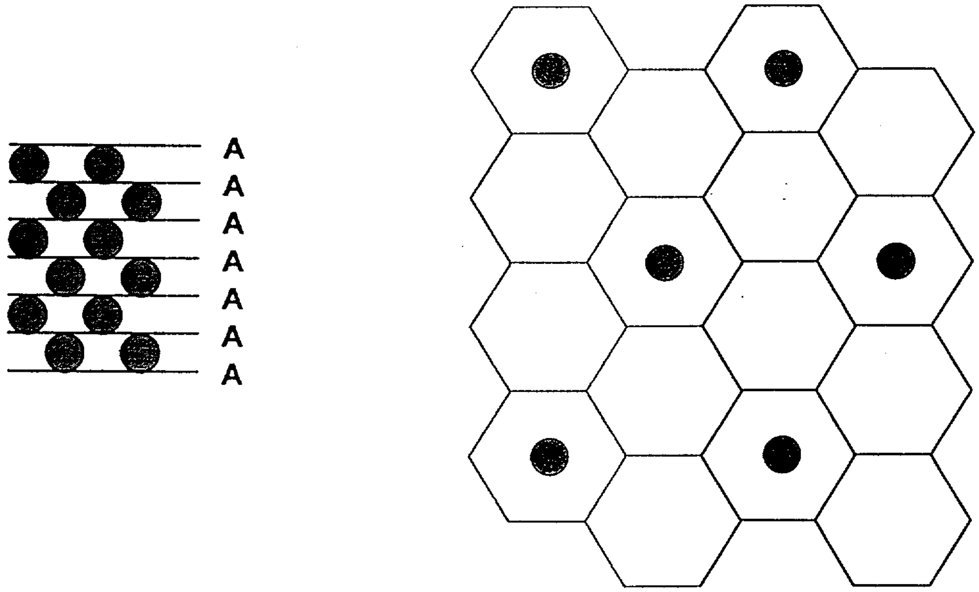


Figure 1. Hexagonal graphite with staggered layers (B layers shown as dashed lines).



(NOT TO SCALE)

Figure 2. Lithium intercalated graphite schematic. All layers aligned.