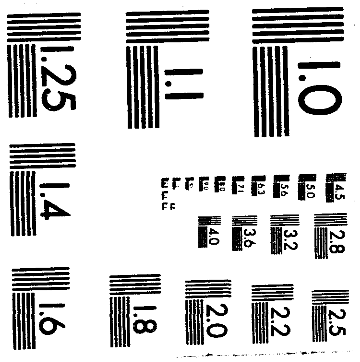
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SAND-93-2761C
Conf-940107--1

REVIEW OF LITHIUM-ION TECHNOLOGY

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Introduction

The first practical use of graphite intercalation compounds (GIC) as battery anodes was reported in a 1981 patent by Basu (1) in which a molten salt cell was described having a negative electrode that consisted of lithium intercalated in graphite. A second patent by Basu, issued in 1983 (2), described an ambient temperature rechargeable system which also utilized lithium intercalated in graphite as the anode. Work in this area progressed at a low level, however, until interest was sparked in 1990 when Sony Corporation announced a new "lithium-ion" rechargeable cell containing a lithium ion intercalating carbon anode. These cells have the advantages of metallic lithium systems; i.e., high energy density, high voltage, and light weight, without the disadvantages of dendrite formation on charge and the safety considerations associated with metallic lithium.

Materials other than carbon have been studied as intercalation anodes (3, 4). Examples are Fe_2O_3, WO_2 and TiS_2. Although these alternate anode materials are of interest academically and for specialty applications, they do not hold much promise for widespread general use due to their increased weight and lower cell voltage.

Studies of cathode materials for lithium-ion systems have centered on the transition metal chalcogenides. A number of these materials are capable of reversibly intercalating lithium ions at a useful potential versus lithium. Both organic liquids and polymers are candidate electrolytes for this technology.

Technology Review

a) Carbon anodes

The crystallinity and micro structure of carbon vary depending on the starting material, the preparation method, and heat treatment. Carbons made at temperatures <1000° C have the most disordered structure. The amount of crystallinity can be increased by heating, and the structure becomes highly ordered at >2200° C, approaching the graphitic structure. A high degree of crystallinity promotes a higher degree of intercalation, while defects, structural imperfections, and disorder generally hinder intercalation. Disordered structure in carbon occurs with small crystallite size and random stacking of adjacent carbon layers, i.e., the layers are basically parallel, but random shifts or rotations are found between adjacent layers. This is known as turbostratic disorder (5).

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

The crystal structure of graphite consists of planar sheets of carbon in a hexagonal pattern that are stacked in registered fashion in the sequence ABABABAB..., known as hexagonal or 2H graphite. Other forms of graphite are known, but are less common. In the 2H graphite, every other layer is aligned, while alternate layers are offset. When lithium intercalates into the graphitic structure, the carbon layers shift to AAAA... stacking, i.e., all layers are aligned. This is because the lowest energy state for the intercalated lithium ion occurs when it is nested symmetrically between two hexagonal carbon arrays. The lithium ions fill the graphitic matrix in stages, the stage number corresponding to the number of graphitic layers which separate two intercalated layers. The theoretical limit occurs at LiC_6, in which lithium ions fill every layer (stage 1 GIC).

In a practical cell, some fraction of the charge passed during lithium intercalation into the graphite anode will be irreversibly lost on the first discharge. This loss is due mainly to the formation of a passivating layer, or solid electrolyte interface (SEI), on the surface of the carbon as a result of electrolyte decomposition reactions. This loss is a function of both the carbon and the electrolyte since the lithium ions are solvated and the solvent molecules tend to co-intercalate with lithium. Insertion of this large aggregate into the graphite causes exfoliation and the generation of more surface area which then becomes passivated. This effect can be reduced by the use of certain cosolvents or complexing agents, e.g., 12-crown-4 ether. The crown ether alters the nature of the solvation sheath around the lithium ion, allowing it to intercalate with minimum co-intercalation of solvent (5). The presence of crown ethers has been shown also to diminish the electrolyte decomposition on the carbon surface, possibly by stabilizing the SEI (6).

Low temperature carbons, e.g., coke, exhibit a relatively small irreversible loss of lithium. This is because these carbons have a large percentage of unorganized structure, and turbostratic shifts exist between each layer of ordered carbon. This disorder limits lattice expansion, thus minimizing solvent co-intercalation. An alternate explanation is that the unorganized regions are able to accomodate some solvent co-intercalation. In either case, exfoliation is avoided. However, the reversible capacity is low, generally $x=0.5$ in Li_xC_6 for cokes, because lithium ions cannot enter the lattice in the orderly staged phases found in graphite. Also, a sloped discharge is observed, consistent with the variation in site energies in the disordered matrix. The high temperature carbons, e.g., graphite, yield high capacities, near $x = 1$ in Li_xC_6, and have flat discharge curves near 0.1 V vs. lithium. However, electrolyte selection must be made carefully to minimize irreversible loss of capacity.

The disorder in some carbons is not readily removed by heat-treatment. Materials made from a polymer precurser have been described that show high capacity approaching LiC_6, but are disordered and exhibit sloping discharge curves (7). A structural model has been developed which accounts for reversible capacity stored in the unorganized regions, as well as the graphitic regions. Therefore, the simplistic view discussed above must be supplemented by more complicated models as we learn more about the relationships between carbon structure and its properties.

b) Cathode materials

Layered lithium metal chalcogenides of the formula $LiMX_2$ and lithium spinel-type materials have been the focus of much attention as lithium insertion cathodes for use with lithium intercalated carbon anodes. The only cathode materials presently known to intercalate lithium ions reversibly at voltages >3.5 V vs. Li are the layered materials $LiCoO_2$ and $LiNiO_2$ and the three-dimensional spinel $LiMn_2O_4$ (8). $LiTiS_2$ has been investigated as a cathode in lower voltage (~2 V) systems (9).

i) *Lithium cobalt oxide*. The $LiMO_2$ compounds have a layered, rock salt structure with lithium and transition metal cations occupying alternate layers of octahedral sites in a distorted cubic close packed oxygen-ion lattice. The layered MO_2 framework provides a two-dimensional interstitial space allowing lithium ions to be easily removed. In the overall 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 $0 \le x \le 0.5$, which yields ~400 Wh/kg at 3.9V for the C/Li_xCoO_2 couple (10). In commercial lithium-ion D size cells, an energy density of 115 Wh/kg has been demonstrated at an average voltage of 3.0 V (78 Wh/kg in a AA cell).

ii) *Lithium nickel oxide*. In the intercalation/deintercalation of lithium ions, the reactivity of Ni^{+4}, like the Co^{+4}, again limits the reaction to $0 \le x \le 0.5$:

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

Assuming an average discharge voltage of 3.5 V, the theoretical energy density of the $C/LiNiO_2$ system is ~350 Wh/kg ($0 \le x \le 0.5$). This should lead to practical cells of ~80 - 100 Wh/kg (10).

iii) *Lithium manganese oxide*. The discharge reactions in manganese oxides involve the insertion of lithium ions into the host structure and diffusion through a network of face-sharing tetrahedra and octahedra with a corresponding reduction of the manganese ions. The lithium can be removed reversibly from $LiMn_2O_4$ to yield λ-MnO_2 at a potential of 4 V vs. Li, or a second lithium can be reversibly inserted at 2.9 V (11). Therefore, the cell reaction utilizing the plateau near 4V is:

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

For practical systems, charging at a constant voltage will allow the removal of 0.73 Li. The theoretical energy density for this couple is ~330 Wh/kg ($0 \le x \le 0.73$), assuming an average discharge voltage of 3.9 V. This should lead to an energy density on the order of 100 Wh/kg in practical cells.

Several defect spinels have also been studied as cathodes for lithium ion cells. The general formula for these materials is $Li_2O \cdot yMnO_2$. Lithium-ion cells containing defect spinel cathodes have demonstrated excellent rechargeable behavior. Stable capacities of >130 mAh/g have been obtained from button cells with both $Li_2Mn_4O_9$ and $Li_4Mn_5O_{12}$ (y = 4 and y = 2.5) cathodes at 0.5 mA/cm^2 (12).

iv) *Lithium titanium disulfide.* In TiS_2, the Ti atoms are 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. Lithium titanium disulfide has good electronic conductivity in both the charged and discharged states, eliminating the need to use a conductive additive in the fabrication of cathodes. Experimental cells have been developed yielding an energy density of 90 - 130 Wh/kg in the AA size . Average discharge voltage is 2.1 V in a sloping profile.

c) Electrolytes

Liquid electrolytes for lithium-ion cells frequently employ a binary mixture of solvents. In order to maximize the electrolyte conductivity, one of the solvents generally has a high dielectric constant, e.g. propylene carbonate (PC), and the other has a low viscosity, e.g. 1,2-dimethoxyethane (DME). The lithium salts that are stable and soluble in these mixtures include $LiAsF_6$, $LiPF_6$, $LiClO_4$, $LiBF_4$, $LiCF_3SO_3$ (triflate), and $LiN(CF_3SO_2)_2$ (imide). A study of the conductivity of solutions of these salts in PC/DME mixtures shows that $LiBF_4$ and triflate have the poorest conductivity and, thus, are not the salts of choice for practical batteries (13). While $LiAsF_6$ and $LiClO_4$ exhibit good conductivity, practical systems avoid these salts because of toxicity and safety considerations. Therefore, researchers have looked to the imide and $LiPF_6$ salts as the solutes of choice. However, studies show that corrosion of the positive collector substrate, particularly Al, can limit applicability of the imide (14). Furthermore, $LiPF_6$ is very reactive and, therefore, difficult to synthesize and handle. Recent tests of an experimental methide salt $LiC(CF_3SO_2)_3$ look promising (14, 15).

The carbon capacity and cyclability are dependent on the electrolyte. For example, PC decomposes on graphite electrodes unless a co-solvent or complexing agent is present (5, 6). The electrochemical stability window of most liquid electrolytes is borderline for use in a 4V cell; those that are stable at the Li potential invariably decompose at the cathode potential. Solid polymer electrolytes are being developed to eliminate the reactivity issues of the liquid electrolyte. One of the most commonly studied materials is poly(ethylene oxide) (PEO) with various lithium salts added (16, 17, 18, 19). Gel systems have been investigated more recently as a means of improving the room temperature conductivity of the polymer electrolytes. The gels are formed by adding a solution of lithium salt in nonaqueous solvent, e.g., $LiClO_4$ in PC, to a polymer network, e.g., PEO, etc. (20). These systems are dimensionally stable and have conductivities approaching those of liquid organic electrolytes.

State of the Art

There is much research in progress on lithium-ion systems worldwide. However, only a handful of companies are producing these batteries. Most of the production is specifically designed for electronic devices, e.g., cellular telephones and camcorders, and therefore little performance data is available. The Sony cell, however, is available for purchase in a two cell battery configuration. The AA size has a room temperature capacity of 400 mAh at the 0.2 C rate, 370 mAh at the C rate, and 330 mAh at the 2 C rate. Energy density is quoted at 78 Wh/kg and 192 Wh/l. 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 (21).

Much work is presently focused on carbon as an intercalation anode. Various types have been studied, and the theoretical limit of LiC_6 (372 mAh/g) has been attained by many. More recent work is aimed at substituting other elements, e.g., boron and phosphorus, into the carbon lattice to increase the reversible capacity (22, 23). Boron is an electron acceptor, and intercalated lithium is an electron donor, therefore, the chemical bond is strengthened. This results in an increased potential of lithium relative to that in pure carbon. The upward shift of potential allows more lithium to be intercalated. Capacities approaching 500 mAh/g have been obtained with this approach. Similarly, phosphorous containing carbons have been reported to exhibit a reversible capacity of ~600 mAh/g. This work suggests that the theoretical geometric consideration of one lithium per six carbons is not limiting. As a greater understanding of substituted carbons is attained, specialty carbons may result in significantly improved lithium-ion cell performance, making this technology the system of choice for many military and consumer applications.

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