

# MODIFICATION OF CARBONACEOUS MATERIALS FOR LI ION BATTERIES

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## INTRODUCTION

The Li-ion battery has received much attention recently because it offers high energy density, safety, and long cycle life [1-12]. Lithium-intercalated carbons are the best choice for the anodes in Li ion batteries for several reasons. First, they are safer than Li metal. Second, carbon is abundant and this lowers the cost of the batteries. Third, the theoretical intercalation capacity of carbon is very high which suggests that high capacity cells could be based on this material. Also, the Li-ion battery has a long shelflife since self discharge is very slow. The lithium-intercalated carbon has a low potential relative to Li metal, so if it is used to replace Li metal, cells with high open circuit voltage are obtained.

Although there are thousands of carbon materials commercially available, so far only a few of them have been successfully used as electrodes for Li intercalation in electrochemical cells with liquid electrolytes. The capacity of the carbon electrode is usually not fully utilized and there is always an irreversible capacity loss associated with carbon electrodes.

Graphite is a good candidate for Li-ion batteries because of its low cost and a long low potential range for Li intercalation. However, the application of graphite has been hindered due to low cycle life. Based on electrochemical and microstructural evaluations, it has been concluded that the exfoliation of graphite and the formation of surface films are the two main causes for failure and irreversible capacity loss [11]. Therefore, the present study will focus on the modification of carbon materials with high capacity and exfoliation resistance.

## EXPERIMENTAL

The surface modification of graphite powders was conducted in the following two ways. First, graphite powders were heated in He-saturated benzene vapor at 1000°C. Second, graphite powders were well mixed in a dilute solution containing phenol-formaldehyde resin and heated until completely dried. Then the dried powders were ground and sieved to a proper size. After this, the powders were heated to 650°C in 10% H<sub>2</sub> in He for two hours to convert the surface-coated polymer to a thin hard, carbon layer which prevents the exfoliation of the graphite grains but allows penetration of Li ions. An alternative way to obtain carbon materials with a graphite structure which have exfoliation resistance is by catalytic carbonization. A small amount of catalyst (nickel acetate) was added in phenol-formaldehyde resin before carbonization. After being heated in an inert

gas at a temperature around 650°C, the carbon materials contain a considerable amount of graphitized structure that is initiated from the catalyst particles, and the overall graphite structure is surrounded by an amorphous carbon matrix. Other modifications to the carbonaceous materials include the doping with heteroatoms and catalytic etching to produce active sites for Li intercalation.

The carbonaceous materials were ground and sieved to fine powders with an average particle size around 30 μm. Thin-film composite electrodes of carbon were prepared by mixing carbon powder and binder (PVDF 10%) and carbon black (10%) and coated onto a Cu substrate.

For electrochemical characterization, the cells were assembled in a He filled glove box with low oxygen and moisture concentration. Li metal foil and LiCoO<sub>2</sub> were used as counter electrodes. 1.0 M LiPF<sub>6</sub> in ethylene carbonate (EC), and diethylcarbonate (DEC) were used as electrolytes. Porous polypropylene thin film (Celgard no. 2400) was used as a separator. Regular constant current charge and discharge cycling and cyclic voltammetry were used to evaluate the performance of the electrodes.

## RESULTS AND DISCUSSION

Graphite powders normally have a thin sheet morphology (c-dimension is much smaller than that of the a-b plane) due to the different bonding between the c-direction and in the a-b plane. When graphite powders are processed as a solid electrode, preferential orientation of the particles (the thin sheets are all aligned parallel to the surface of the electrode) should be expected. This causes low rates of intercalation and disintercalation because Li ions enter at the edge sites or at defects in the layers.

Figure 1 shows an SEM micrograph of a prepared electrode. It can be seen that with the precoating process, graphite grains are bonded to form rounded particles. Therefore, in the final coated electrode prepared by this process, graphite grains have a random orientation rather than a preferred orientation with the basal plane parallel to the surface. Figure 2 shows the potential-capacity of a coated sample. The curves consist of two parts which correspond to the contributions from both the graphite and the carbon coating. Preliminary data show this kind of carbon is more stable in terms of cycling.

In Li-ion batteries, the electrodes are prepared by coating electroactive particles onto current collectors. Therefore,

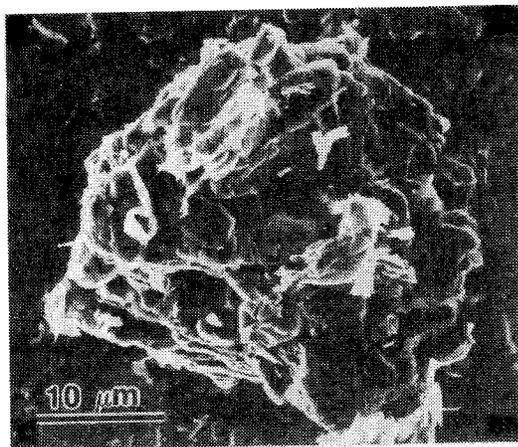
electrode coating plays a crucial role in determining the performance because: (1) It is desirable to maximize the content of the active materials to retain the capacity of the electrode. This means that the binder concentration cannot be too high and (2) the lattice of the electrode active materials may change by 10% during charging and discharging which corresponds to a volume change up to 30%. Therefore, during intercalation the grain size increases while during deintercalation of Li the grain size decreases and this causes the loss of the contact between nearby grains. This phenomena is not only associated with the anode (carbon electrode) but also for the cathode. Large irreversible capacity loss for carbon electrodes might arise from surface film formation, in addition to the loss of contact of the grains of the electrode materials. In a packing structure consisting of equal-sized spherical particles, each of the particle will contacts up to eight nearest neighbors. While for irregular-shaped particles, the average number of contacts with the nearest neighbor particles is less than 5 on average. Our current work aims to reduce the irreversible capacity loss through reshaping the carbon particles and using highly elastic binder to improve the coating technology.

### SUMMARY

In summary, we have present in this paper the modifications of carbon materials as anodes for Li-ion batteries. It has been found that with the surface and microstructure modification the electrochemical properties and durability of the prepared carbon electrodes have been significantly improved.

### ACKNOWLEDGMENTS

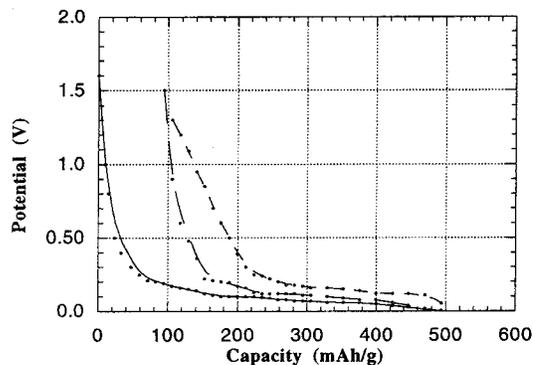
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**Figure 1.** SEM micrograph of a carbon coated and bound graphite particle in which graphite powders have random orientation.

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**Figure 2.** The Potential of the coated graphite electrode versus Li intercalation capacity (10.1 mA/cm<sup>2</sup>).