

## Flexible graphite as battery anode and current collector

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### Abstract

In making graphite-based electrodes and current collectors, there is significant simplification if a flexible graphite process is used. The lithium intercalation capacity of Grafoil<sup>®1</sup> flexible graphite sheet and its powder was evaluated using electrochemical charge–discharge cycling in half-cell configuration (coin cell with Li anode and graphite cathode). The sheet form was used with and without a copper current collector. Excellent electrical conductivity of the monolithic material with very low interface resistance helps as current collector and electrode. The comparatively low capacity of Grafoil<sup>®</sup> sheet is thought to be due to diffusion limitation of the structure, especially in the light of the very high capacity of its powder form. The highly irreversible capacity of the powdered material may be due to unfunctionalized graphitic structures or impurities present in the powder. Impedance response for the first intercalation–deintercalation was different than responses taken after several cycles. The presence of a second impedance arc suggests structural modification is taking place in the graphite anode, possibly through formation of a porous structure as a result of graphite expansion.

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### 1. Introduction

The continuing demand for lighter and smaller mobile electronics, especially notebook PCs and cellular phones, has driven the development of higher capacity Li-ion batteries. Similarly, the growing interest in hybrid electric vehicles has put emphasis on the development of new anode materials that are safe and have high energy density [1–3]. This intense search for alternative anode materials capable of intercalating larger amounts of lithium has led to the synthesis of many unique disordered carbon materials [4]. Having good cycling capabilities with high reversible and low irreversible capacity is required to increase volumetric as well as gravimetric energy density of Li-ion batteries [5–8]. Materials should also be able to carry high discharge rates without any safety is-

sues or performance degradation. Flexible graphite sheet may provide some unique features for these requirements.

Flexible graphite is made from natural graphite flakes. In each planar array, or graphene layer, the carbon atoms are covalently bound quite strongly, nearly  $710 \text{ kJ mol}^{-1}$  [9]. In contrast, the attractive force between the planes is very weak, perhaps only a few  $\text{kJ mol}^{-1}$ . The result is a structure that is very strong in the direction of the plane, but very weak perpendicular to the plane. Expanded graphite is obtained by intercalation of anions into graphene layers of natural graphite and exfoliation of stage compound at high temperatures. The force of the expanding intercalant causes the layers to push apart and grow in the thickness direction. The result of the expansion is a vermicular form of graphite, or exfoliates, commonly referred to as ‘worms’. Resulting worms have 100–1000 times the volume of starting material depending on the exfoliation conditions. As with graphite flake, the worms exhibit anisotropic characteristics. Compression of the worms results in a continuous, binder-free flexible graphite sheet that can be manufactured in a variety

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<sup>1</sup> GRAFOIL is a registered trademark of Advanced Energy Technology Inc.

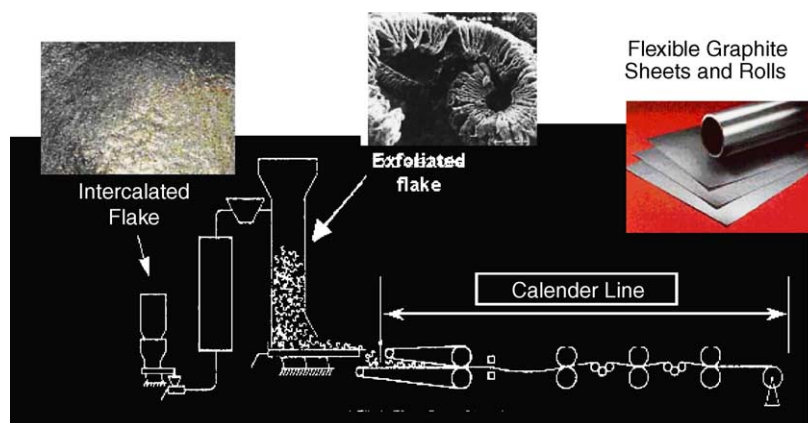


Fig. 1. Flexible graphite manufacturing process from flake intercalation to formation of sheet and rolls.

of thicknesses and densities. A schematic of flake, exfoliate, sheet and the manufacturing process is shown in Fig. 1. The anisotropy of the worms is carried over to the flexible graphite sheets. The plane of the sheet reflects the stronger bonding within the layers of the parent graphite crystallites, while the sheet thickness is weaker. Anisotropy of flexible graphite can be particularly useful because the material can behave rigidly in one direction and compressible in the perpendicular direction; permeable in one and impermeable in the other; relative insulator in one direction and a very good conductor in perpendicular direction. In reference to the ability of graphite to resist corrosion or attack in aqueous systems, no other conductive material except gold and platinum is considered more passive than graphite.

Flexible graphite has enhanced mechanical, thermal and electrical properties to accommodate the requirements of various applications in liquid and gas environment. It is chemically very stable against corrosion, highly electrically conductive and transfers heat effectively. It is very light, flexible, compressible and conformable. The properties of flexible graphite are shown in Table 1. These physical attributes of flexible graphite allow it to be fabricated into a variety of shapes and sizes giving design flexibility. Historically, these

properties of flexible graphite sheet have made it an excellent gasket material for industrial and automotive sealing applications. More recently, these properties have made flexible graphite the material of choice for fuel cell flow field plate components.

In this study, the intercalation and deintercalation behavior of Grafoil® flexible graphite is examined to determine its suitability for use as an anode material and current collector at the same time for lithium ion batteries. Sheets made from expanded graphite or expanded graphite powder may provide improved electrical capacity and better thermal characteristics than other carbon-based anode materials. It is known that flexible graphite can have thermal conductivity rivaling copper. This property may allow flexible graphite-based anodes to overcome heat dissipation issues for high discharge conditions, a necessary requirement for high current drain and transportation applications. In addition, the high volume sheet manufacturing process used to make flexible graphite may provide a simpler and more cost effective way to produce anode components.

## 2. Experimental

Grafoil® flexible graphite sheet and a powder made from the sheet were included in this evaluation for their lithium intercalation–deintercalation performance. Sheets were made from natural graphite flakes with a purity of 99.8% carbon. Natural graphite flakes were reacted with solutions of nitric and sulfuric acid to produce graphite intercalation compounds, which were then washed with water and air-dried. The resulting residue compounds were then exfoliated in a lab furnace at high temperature. The exfoliated graphite ‘worms’ were then compressed into foils with a thickness of 0.275 mm and a density of  $0.8 \text{ g cm}^{-3}$ . Powders were obtained by shredding sheet material and then jet-milling to obtain particles with an average size 90% less than  $30 \mu\text{m}$  particles.

Sheets of flexible graphite material were punched out to provide samples suitable for testing as coin cells (2032 but-

Table 1  
Typical material and physical properties for Grafoil flexible graphite

Property	Value
Density	$0.2\text{--}1.5 \text{ g cm}^{-3}$
Carbon content	>99%
Sulfur content	500 ppm
Chloride content	<20 ppm
Compressibility	43%
Recovery	15%
Sealability	$0.5\text{--}10000 \text{ ml h}^{-1}$
Tensile strength	>4 MPa
Compressive strength	>200 MPa
Modules of elasticity	>1000 MPa
Operational temperature	$-240\text{--}3000 \text{ }^\circ\text{C}$
Electrical conductivity	$10\text{--}1000 \text{ mS cm}^{-1}$
Thermal conductivity	$5\text{--}140 \text{ W mK}^{-1}$
Thermal expansion	$(-0.4 \text{ to } 27) \times 10^{-6} \text{ W m}^{-1} \text{ K}^{-1}$

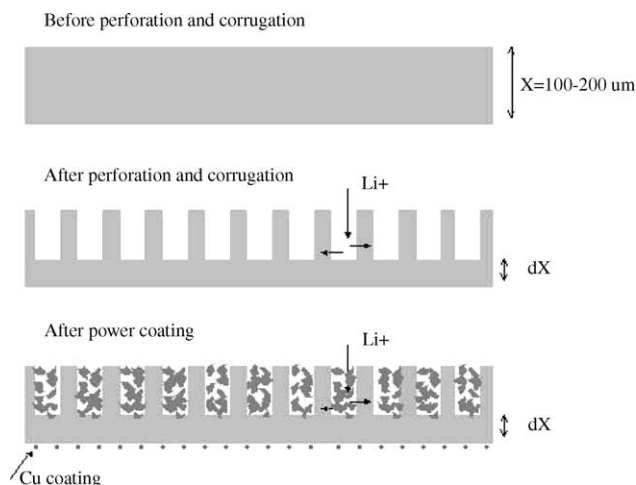


Fig. 2. Some approaches using flexible graphite sheet as current collector/electrode combination in lithium ion battery application.

ton cell). Samples were assembled with and without a copper current collector. Preparation of graphite anodes from powder involved mixing 70–90% graphite with 10% PVDF binder and 10% carbon black in the presence of 1-methyl-2-pyrrolidinone (NMP). This mixture was tape-casted onto a 20–30  $\mu\text{m}$  thick copper foil with a 200  $\mu\text{m}$ -space blade. Green electrodes were placed in an oven for overnight drying. Punched samples of both foil and powder/collector were placed in a vacuum oven for another overnight drying before assembly in a glove box into 2032 size coin cells. Polyethylene/polypropylene micro porous membrane (Celgard 2300) wetted with the electrolyte [1 M  $\text{LiPF}_6$  in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC)] was used as the separator. Cycling and AC impedance measurements were taken using a battery cycler and Solartron 1287 and 1260 electrochemical interface and impedance analyzer. Measurements were carried out at room temperature outside the glove box under various charge and discharge conditions. AC impedance data were taken between various stages of charge and discharge cycles. Each cell was allowed to rest at the open-circuit potential for 30 min between measurements. Amplitude of 5 mV versus the open-circuit potential was used for the impedance measurements in the frequency range between 100 kHz and 100 MHz.

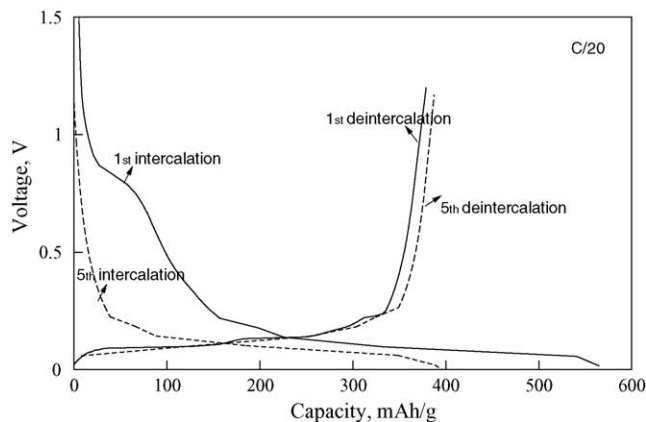


Fig. 4. The first and fifth intercalation–deintercalation cycles for milled expanded graphite powder electrode at  $C/20$  rate.

### 3. Results and discussion

Chemical stability of flexible graphite makes it useful as a component in supercapacitor devices, batteries, as well as fuel cells. It can be combined with other materials as an electrode/current collector combination with and without binder for lower interface resistances. In such an approach, flexible graphite can be a standard solid sheet or a perforated mesh material as shown in the Fig. 2. The electrical and thermal conductivity of flexible graphite makes such combinations very favorable.

Two different types of samples were utilized in the experiments. Fig. 3 shows scanning electron micrographs (SEM) of an exfoliated graphite flake, compressed graphite foil, and a jet-milled, expanded graphite powder. The jet-milled material had an apparent density of only  $0.8 \text{ g cm}^{-3}$ , and a surface area of  $23 \text{ m}^2 \text{ g}^{-1}$ . For comparison, the compressed sheet material has an apparent density of  $1.12 \text{ g cm}^{-3}$  and a surface area of approximately  $20 \text{ m}^2 \text{ g}^{-1}$ .

Fig. 4 shows the first cycle behavior of the powder obtained from milled, compressed sheet, acquired at a rate of  $C/20$ . The highest first cycle intercalation capacity for the powder was  $574 \text{ mAh g}^{-1}$ . This sample also had very high irreversible capacity ( $195 \text{ mAh g}^{-1}$ ). In addition to edge plane reactivity, a portion of this high irreversible capacity may be associated with impurities reacting with electrolyte and

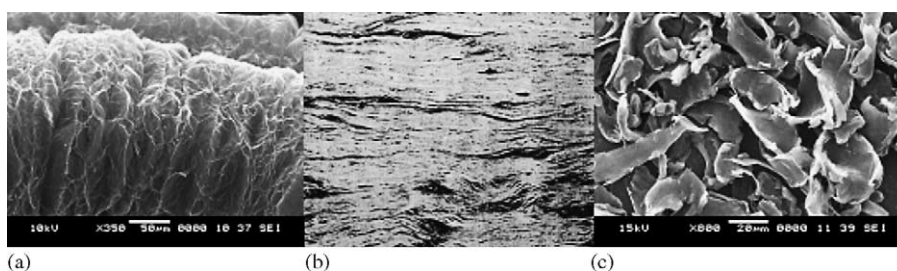


Fig. 3. SEM micrograph of (a) exfoliated graphite, (b) compressed sheet and (c) milled powder.

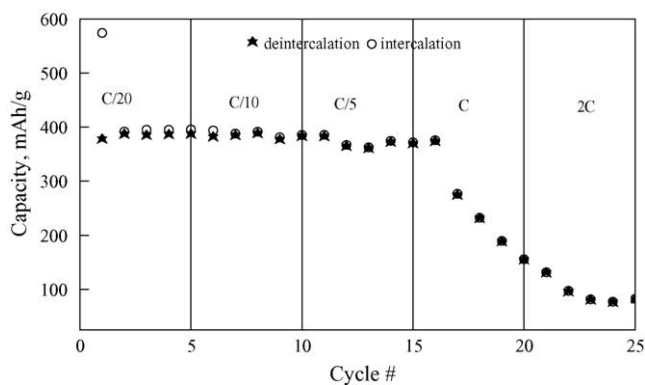


Fig. 5. Milled expanded graphite powder electrode capacity for five cycles at  $C/20$ ,  $C/10$ ,  $C/5$ ,  $C$  and  $2C$  rates.

lithium. In comparison to common commercial materials, the powder had high surface area and smaller particles, contributing factors to high irreversible capacity (usage of lithium by solid–electrolyte interface (SEI) formation and other side reactions). Another possibility for such a high irreversible capacity is the contribution coming from exfoliation of the expanded graphite structure in the presence of organic electrolyte. On the first intercalation cycle, potential levels off around 850 mV. This is always seen on the first cycle no matter what the charge–discharge rate and the material is. This is often assigned to the exfoliation of graphite in the presence of electrolyte. Flexible graphite is advantageous in this respect due to prior exfoliation of structure. Double or triple exfoliation may eliminate this potential leveling with capacity to low levels.

Following the first cycle, capacity was very stable for both charge and discharge cycles. Fig. 5 shows rate capability of the powder at consecutive charge–discharge cycles. It was confirmed that the milled powder was able to carry high discharge rates far better than some other graphite materials [6].  $C/20$ ,  $C/10$  and  $C/5$  rates gave capacities very close to each other. After a  $2C$  discharge rate, the coin cell was cycled at a  $C/10$  rate and almost complete recovery was observed. Lithium intercalation and deintercalation into the graphite structure with different stages are clearly defined in differential capacity data (Fig. 6). Three distinct peaks are observed

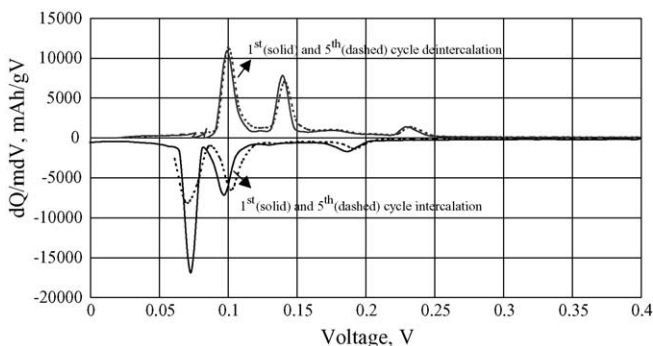


Fig. 6. Differential capacity plots for milled expanded graphite powder-based coin cell for first and fifth charge–discharge cycles at  $C/20$  rate.

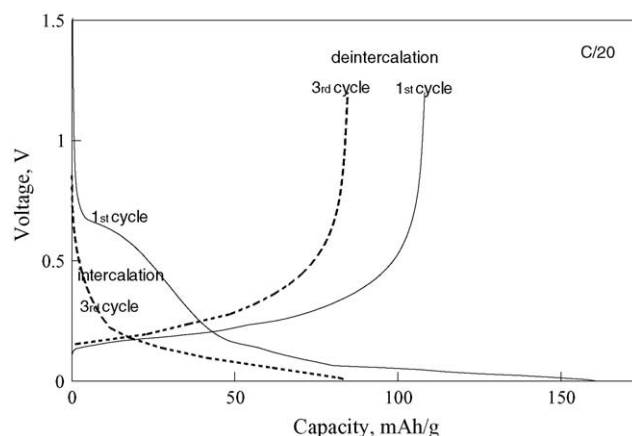


Fig. 7. Subsequent charge–discharge of flexible graphite cell without copper current collector. First and third cycles at  $C/20$  rate.

at 0.18, 0.1 and 0.07 V during intercalation. Peak sharpness and separation was the best with expanded graphite material compared to artificial graphite, implying distinct phase separation from one lithiated stage to another [6].

In the new sets of experiments, cells were assembled with flexible graphite sheet as intercalation electrode without any current collector. Fig. 7 shows first three cycle data when at  $C/20$  rate. First cycle gave low reversible capacity with capacity fading after second and third cycles indicating instability of interfaces. Fig. 8 was obtained with the same cell at a very low rate,  $C/100$ . The capacity was improved about five times. While such a low rate may not be practical, it was a quick way of checking structural limitation of the tested material to the fast diffusion of lithium ions. The layered structure of the compressed flexible graphite had limited that process. There was no capacity decay between consecutive cycles implying structural stability for the intercalation–deintercalation process. Average capacity was about 30% of the theoretical capacity of lithium intercalation. Considering that this work was carried out using off-the-shelf material with no optimization of porosity or thickness, these are encouraging results for further investigation.

AC response for flexible graphite-based electrode before and after intercalation and deintercalation is presented in

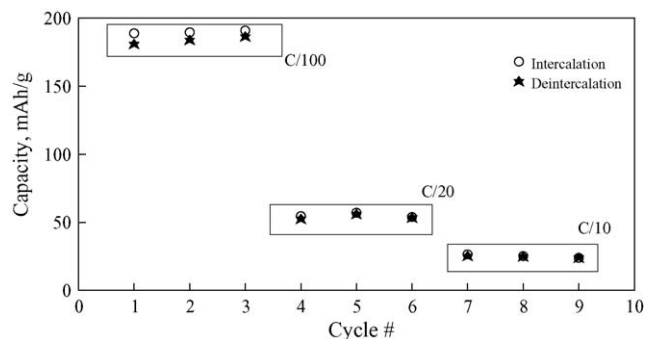


Fig. 8. Lithium intercalation–deintercalation capacity of flexible graphite sheet at  $C/100$ ,  $C/20$  and  $C/10$  rates for three cycles.

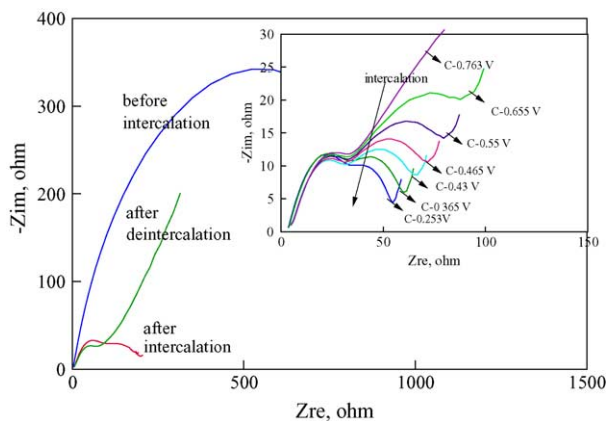


Fig. 9. Impedance response of flexible graphite sheet after (a) first cycle at  $C/20$  rate and (b) multiple cycles at  $C/20$  rate.

Fig. 9. AC impedance response was useful to show structural differences between the powder and sheet forms of intercalation electrodes. The absence of a separate conductive current collector was reflected in the AC impedance response. Total system impedance was very high for the new cell before intercalation, but was reduced following full lithium intercalation into graphite structure. This change was due to staging of graphite with continuous lithium insertion/deinsertion into and from graphite by migrating through a newly formed SEI layer. This type of impedance reduction was typical for both powder and sheet material. Clear separation of time constants was observed following the first intercalation cycle. Two semi-circles, implying finite diffusion processes through a layered or porous structure, are formed at low- and high-frequency range. The high-frequency portion of the circle was not changing much as a function of intercalation capacity (Fig. 10). This may be due to the stable nature of the SEI layer that is not intercalation potential dependent. But the low frequency portion of the semi-circle has given lower impedance. When graphite was fully deintercalated, the sec-

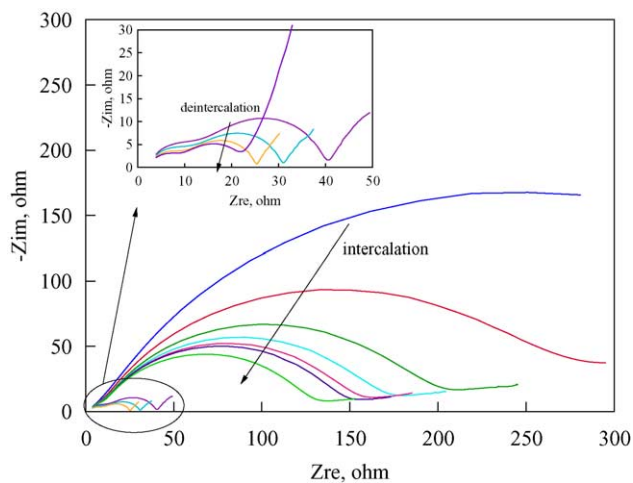


Fig. 10. First cycle impedance response of milled expanded graphite powder at  $C/20$  rate.

ond semi-circle disappeared in sheet material. The very low frequency portion of the response is considered to come from diffusion limitations during the intercalation process. At both extremes of intercalation and deintercalation, the response at low frequencies was capacitive due to over-intercalation and over-deintercalation. Although the magnitude of the semi-circles had changed, the slope of the very low frequency response was very much constant throughout the process. Multiple charge–discharge cycles caused the structure to develop a much more porous structure than the starting material (Fig. 10). Since cells made from flexible graphite did not use a separate current collector, impedance was higher than for cells composed of powder-based electrodes. It may be necessary to coat the current collection side of the flexible graphite by sputtering, a common practice for coating supercapacitor electrodes, in order to negate these effects.

#### 4. Conclusions

Sheets of flexible graphite and powders made from the flexible graphite sheet were tested for their performance as Li-ion battery anodes. Graphite powder made by jet-milling flexible graphite showed very high reversible capacity compared to its foil form. This indicates that the inherent nature of the natural graphite exfoliate does not limit lithium intercalation capacity. In contrast, the layered structure of flexible graphite foil acts to hinder permeability of electrolyte and ion transfer, and limits the effectiveness of typical graphite foils as a battery anode. Structure modification to the foil that improves the permeability of electrolyte and lithium ions could dramatically improve performance, while maintaining the processing and manufacturing advantages of flexible graphite.

The high irreversible capacity observed for the natural graphite powder is like a result of impurities and the high surface area of the samples. Both of these attributes can be addressed in subsequent studies: impurities through a combination of thermal and chemical processes, and particle size by a choice of starting material and milling conditions. Surface area reduction may also help in improving the thermal behavior of the fully lithiated graphite anodes. These and other characteristics of natural graphite foils and powders would be considered for further evaluation and development of these materials.

Ease of manufacturing a continuous anode sheet without having any binder in the structure with right combination of thickness and porosity should reduce the cost of anode manufacturing and increase production speed and packaging. Excellent thermal properties compared to powder form should also help to overcome heat dissipation issues for high discharge conditions, a necessary requirement for high current drain and transportation applications. Similarly, the material is an excellent current collector for the same application due to inertness in corrosive environments and excellent electrical and thermal properties.

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