Low Cost Carbon Electrodes For Batteries and Fuel Cells

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Abstract

The primary objective of this Phase I program was to demonstrate the development of a low cost, carbon fiber obtained from domestic pitch-based sources as anode material for rechargeable lithium-ion batteries. The demonstration includes development of several half-cells and evaluation of reversible specific capacity and irreversible capacity loss of the developed anode material. Several prismatic design prototype lithium-ion cells were also developed with the chopped carbon fiber anode material and evaluated these cells for cycle life and deliverable capacity at different discharge rates.

The specific objectives of Phase I work were to (1) prepare low cost carbon fiber anode, (2) analytically characterize the anode material, (3) develop half-cells with lithium metal counter electrodes and evaluate reversible capacity and irreversible capacity loss for lithium-ion intercalation and de-intercalation, (4) develop prototype lithium-ion cells with the developed carbon fiber anode and commercially available cathode materials, and (5) evaluate performance and assess technical feasibility.

All the tasks were successfully completed and the project goal was fully achieved. In this program, we studied low cost carbon fiber from a domestic source as an anode material in half-cell configuration and evaluated reversible capacity and irreversible capacity loss in carbonate-based 1M $LiPF_6$ electrolyte. A reversible capacity of as high as 340 mAh/g was observed for lithium-ion intercalation and de-intercalation with the developed carbon fiber. An irreversible capacity loss of 4% was observed. These values are superior to those obtained from the industry standard carbon material (MCMB carbon currently available only from Japan) presently used in commercial lithium-ion batteries.

We also tested the developed carbon fiber anode against commercially used cathode material in prototype lithium-ion pouch cells and evaluated the performance with respect to cycle life and deliverable capacity at different discharge rates. Excellent cycling behavior and rate capability was observed.

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I. INTRODUCTION

Since its introduction and commercialization in 1991, lithium-ion battery systems have received considerable interest not only to the battery community but also to the academia and electronic industries. This is mainly due to their several advantageous characteristics over the competing technologies (e. g., Pb-acid, Ni-Cd and Ni-MH) such as high specific energy (~160 Wh/kg), long cycle life (~500 cycles with 80% capacity retention), low self-discharge (~8% per month), and environmentally compatible. Lithium-ion batteries are now widely used for consumer electronic applications such as cellular phones, laptop computers, and camcorders. Currently, these batteries are mass-produced only in Asia (Japan, China, and Korea) and available in the U. S. through Asian manufacturers.

In lithium-ion batteries, carbon is used as an anode, a lithiated transition metal intercalation compound as a cathode and $LiPF_6$ as an electrolyte in carbonate-based organic solvents. The reactions at the electrodes and overall cell reaction are

$$\text{Cathode} \qquad LiMO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\Leftrightarrow}} Li_{1-x}MO_2 + xLi^+ + xe$$

$$\text{Anode} \qquad C + xLi^+ + xe \overset{\text{charge}}{\underset{\text{discharge}}{\Leftrightarrow}} Li_xC$$

$$\text{Overall} \qquad LiMO_2 + C \overset{\text{charge}}{\underset{\text{discharge}}{\Leftrightarrow}} Li_xC + Li_{1-x}MO_2$$

where $LiMO_2$ represents the lithiated metal oxide intercalation compound.

The electrochemical process is the uptake of lithium ions at the anode during charge and their release during discharge, rather than lithium plating and

stripping as occurs in metallic lithium rechargeable battery systems. As metallic lithium is not present in the cell, lithium-ion cells have enhanced safety and a longer cycle life than the cells containing metallic lithium.

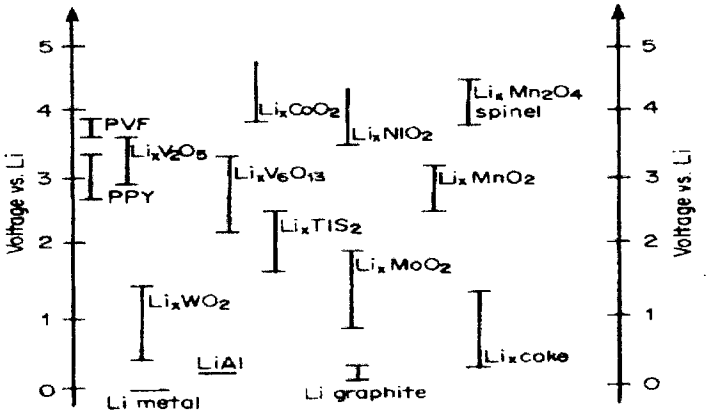


Fig. 1: Electrochemical Potential of Some Lithium Intercalation Compounds vs. Lithium metal. PPY = Polypyrrole; PVF = Polyvinyl furan.

Hard carbon (1) and graphite (2) are used as anodes in lithium-ion batteries. The carbon materials deliver a reversible capacity of ~370 mAh/g corresponding to the chemical formula LiC_6. The electrochemical potential of lithiated carbon is almost the same as that of metallic lithium as shown in Figure 1 (3). Thus, an electrochemical cell made with a lithiated carbon material will have almost the same open-circuit voltage as one made with metallic lithium. In practice, lithium-ion cell is manufactured in a fully discharged state with carbon and lithiation of the carbon is carried out by subsequently charging the cell.

During the first electrochemical intercalation of lithium into the carbon, some lithium is irreversibly consumed and a significant amount of capacity can not be recovered in the following discharge. This irreversible capacity loss, which depends on the electrolyte solution and the type of carbon material, is explained on the basis of the reduction of the

electrolyte solution and the formation of a passivating film (SEI layer) at the Li_xC interface (4). Chemical combination of lithium to the active surface functional groups of carbon may also play an important role in this irreversible capacity loss (3).

The state-of-art lithium-ion cells use some special-type of carbon materials that are only produced in Japan. The Japanese carbon materials provide high reversible capacity (~330-340 mAh/g) and low irreversible capacity loss (≤10%) but are expensive (~$50/kg). The identification of relatively low cost domestic source of carbon anode that can deliver comparable reversible capacity and irreversible capacity loss would be of critical importance. This program focuses on the development of such carbon anode material.

II. EXECUTIVE SUMMARY

The primary objective of this Phase I program was to demonstrate the development of a low cost, carbon fiber obtained from domestic pitch-based sources as anode material for rechargeable lithium-ion batteries. The demonstration includes development of several half-cells and evaluation of reversible specific capacity and irreversible capacity loss of the developed anode material. Several prismatic design prototype lithium-ion cells were also developed with the chopped carbon fiber anode material and evaluated these cells for cycle life and deliverable capacity at different discharge rates.

The specific objectives of Phase I work were to (1) prepare low cost carbon fiber anode, (2) analytically characterize the anode material, (3) develop half-cells with lithium metal counter electrodes and evaluate reversible capacity and irreversible capacity loss for

lithium-ion intercalation and de-intercalation, (4) develop prototype lithium-ion cells with the developed carbon fiber anode and commercially available cathode materials, and (5) evaluate performance and assess technical feasibility.

All the tasks were successfully completed and the project goal was fully achieved. In this program, we studied low cost carbon fiber from a domestic source as an anode material in half-cell configuration and evaluated reversible capacity and irreversible capacity loss in carbonate-based 1M $LiPF_6$ electrolyte. A reversible capacity of as high as 340 mAh/g was observed for lithium-ion intercalation and de-intercalation with the developed carbon fiber. An irreversible capacity loss of 4% was observed. These values are better than those obtained from the carbon material (MCMB carbon) presently used in commercial lithium-ion batteries.

The electrode thickness and heat-treatment temperature plays significant roles in obtaining higher reversible capacity and lower irreversible capacity loss. The thinner electrode and higher temperature treatment provides better lithium-ion intercalation/de-intercalation behavior.

We also tested the developed carbon fiber anode against commercially used cathode material in prototype lithium-ion pouch cells and evaluated the performance with respect to cycle life and deliverable capacity at different discharge rates. Excellent cycling behavior and rate capability was observed.

III. EXPERIMENTAL

A. Chemicals and Materials

A high purity grade propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) were obtained from Grant Chemicals. A different combination of these solvents was used as received to prepare 1M $LiPF_6$ electrolyte in a glove box. $LiPF_6$ salt was purchased from Hashimoto Chemicals. The electrolyte solution was used as received. Copper foil (0.02 mm thick) and aluminum foil (0.04 mm thick), purchased from A. J. Oster, were used as substrates for the negative (anode) and positive (cathode) electrodes, respectively. Lithium metal foil of 50 μm was obtained from Foote Mineral. $LiCoO_2$ (obtained from FMC) was used as positive electrode material for the development of prototype lithium-ion cells. The carbon electrode materials were chopped carbon fiber from Conoco and pitch-based carbon fiber tow from Amoco. Celgard 2400, purchased from Hoechst Celanese, and polyethylene Tonen separator from Exxon Mobile were used as separators. The binder material was polyvinyledene fluoride (PVDF, obtained from Elf Atochem). Dimethyl formamide (DMF, Aldrich) was used as a solvent to dissolve PVDF. Soft plastic "White Bag" from Shield-Pack, Inc. was used as a packaging material for pouch cells. The "White Bag" is made with 3-layers of foils: aluminum foil is laminated in between white plastic foil at the top and a colorless plastic foil at the bottom.

B. Processing to Produce Carbon-Carbon (C-C) Electrodes

It has been determined for the electrode/anode in a lithium-ion battery made of C-C to properly function, it's thickness must be less than 120 μm and preferably less than

100μm (≈ 0.004 inches) thick. Heretofore, C-C in such thin cross sections had not been produced. It was, therefore, necessary to develop processing methodology to produce very thin C-C composites.

In order to achieve the required high electrical conductivity, pitch base fiber is required as the reinforcement. In this case, two fiber types were investigated that consisted of P30X from Amoco and the discontinuous _ to 3-inch staple lengths from Conoco. Both fibers are produced from petroleum pitch and have an approximate diameter of 10μm. The P30X is a continuous 2k tow and the Conoco is the discontinuous random staple material.

Also, to achieve a high electrical conductivity of C-C composite, a graphitizable matrix must be used which must be derived from a pitch. WVU coal extract pitch (CEP) was utilized, since it is known to be a good binder pitch, as well as graphitizable. For lithium-ion batteries, any impurities will dramatically and adversely affect efficiency and irreversible capacity of the battery. Thus, the CEP was purified as developed in the CPCPC Fiber Program, which consists of solvent extraction and filtering of the extract to remove the insoluble ash impurities. Some organic sulfur remains in the pitch but is volatized in subsequent graphitization. The solvent extract pitch was separated from the solvent by vacuum distillation and the remaining pitch ground to approximately minus 100 mesh. The pitch particles are heated in air and subsequently slurred with a dilute phenolic-alcohol mixture.

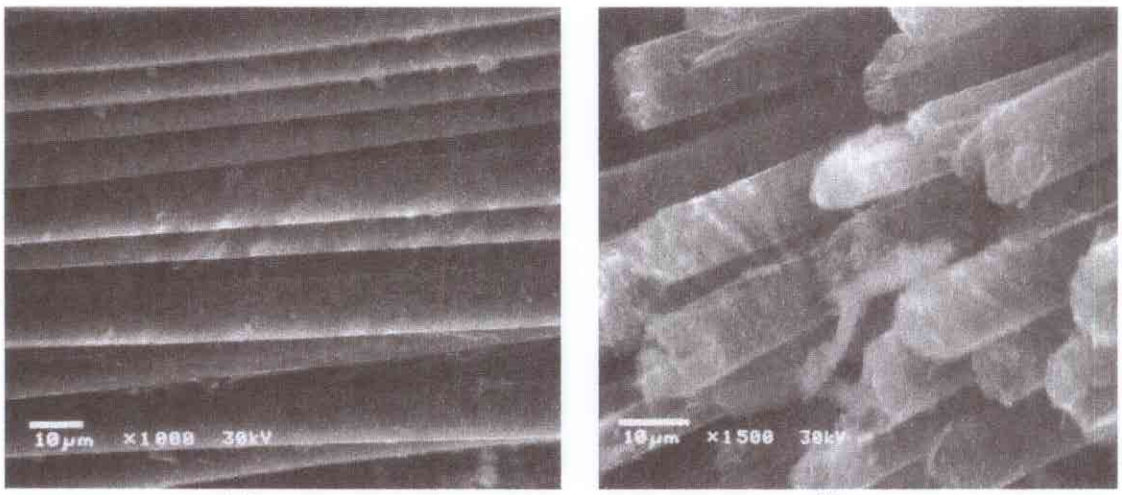
The pitch fibers are spread to achieve a thin layer of approximately 100 - 150μm. The spread pitch fibers are placed in a steel die and the slurry poured over the fiber array. The die is closed with pressure up to a few thousand psi with heat applied, the phenolic cures and holds the fibers in place, followed by the pitch becoming a liquid to fully form the matrix. Heating of the die is continued until at least 400°C is achieved up to as high as 550°C, which cokes the pitch binder. This pressure molding produces the required thin composite that is flat and uniform thickness.

The molded thin plate is then placed between graphite block to maintain flatness and heated to graphitize the matrix, as well as assure the pitch base fibers are exposed to high temperatures that maximize electrical conductivity. Heat treating temperatures of approximately 2900°C have been performed.

Significant iterative development was required to make C-C composite anodes at 100μm or below in thickness that had complete integrity and remained flat for suitable use as a lithium-ion battery electrode. Among the attributes of the C-C composite anode are that it is reusable or recyclable, as well as safety which is of considerable significance. During this year commercial petroleum based pitch fibers were used as the reinforcement, with most effort directed to establishing the methodology for fabricating an acceptable less than 100 μm thick electrode. It is intended in the coming year to utilize coal tar pitch based fiber from the CPCPC Fiber Program that will result in the best quality electrode fabricated completely from coal derived materials.

C. *Characterization of Carbon Fiber Electrode Material*

The carbon composite electrode materials were characterized by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) technique. The in-plane and cross-sectional views of the C-C composite are shown in Fig.2 (a) and (b), respectively. The



(a) (b)

Fig. 2: SEM images of Composite Electrode (a) in-plane, (b) cross-section

composite is composed of disordered carbon fibers.

Figure 3 shows a comparison of the X-ray diffraction patterns of the C-C composite with

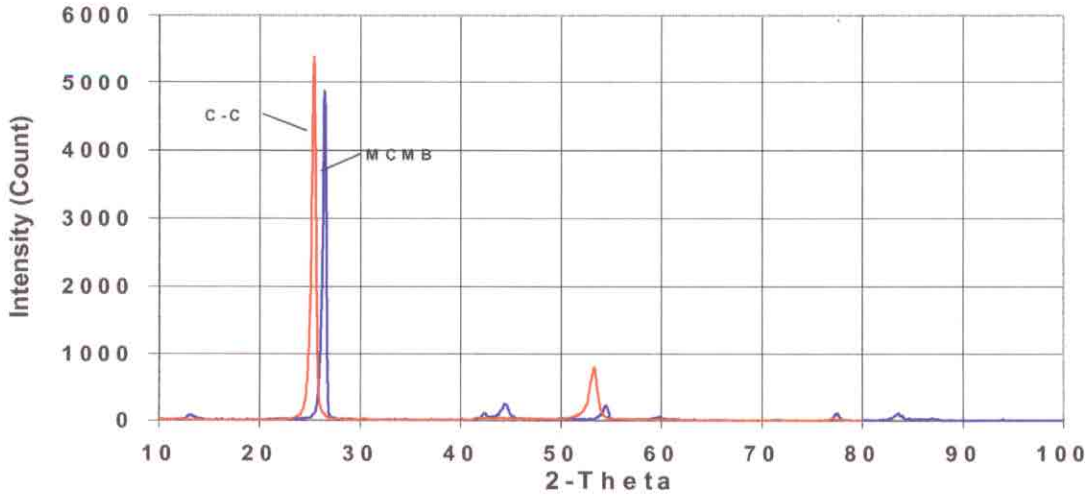


Fig. 3: X-ray Diffraction Patterns of C-C Composite and MCMB Carbon

MCMB carbon. The d_{002} spacing of the C-C composite and MCMB are 0.349 nm and 0.337 nm, respectively. The higher interlayer spacing of the composite electrode allows lower expansion during lithium-ion intercalation.

D. Electrodes Preparation

i. Lithium Electrode

Expanded nickel mesh of 3 μm thick (Delker Corporation) was cut to the size of lithium electrode (2.5 cm x 3.5 cm) with an attached tab (6.3 mm wide and 19 mm long). Both sides of the expanded mesh were cleaned with acetone. The substrates thus prepared were transferred to a glove box (H_2O < 1 ppm) where metallic lithium of 50 μm thick (Foote Mineral) was press fitted to the substrates. The developed lithium electrodes were used as counter electrodes for half-cells measurements.

ii. Carbon Fiber Electrode

As prepared composite plate was cut to a desired electrode dimensions (2.5 cm x 3.5 cm for half-cells and 5.0 cm x 6.25 cm to 13.0 cm x 19.0 cm for lithium-ion cells) and nickel foil was riveted to one edge of the plates. The resulting electrodes with nickel tabs were used as working electrodes for half-cells and anodes for lithium-ion cells studies.

iii. $LiCoO_2$ Electrode

A slurry of 85% $LiCoO_2$ (FMC Corporation), 7% carbon black (Chevron Chemical Corporation), and 8% Poly(vinylidene fluoride), PVDF (Aldrich) was prepared in 1-methyl 2-pyrrolidinone, NMP (Aldrich) and coated on aluminum substrate (40 μm thick). The coated substrate was dried over hot air. It was then cut to the size of the positive electrodes (5.0 cm x 6.25 cm to 13.0 x 19.0 cm) with attached tabs for lithium-ion cells.

The resulting positive electrodes were pressed, vacuum dried and stored in a desiccator prior to use.

E. Development of Cells

i. Half-cells

Several half-cells were made according to the following configuration:

Lithium electrode (Li)/Separator (S)/Carbon Fiber electrode (C)/Separator (S)/Lithium electrode (Li)

The carbon fiber electrode was bagged with Celgard 2400 separator. The bagged working electrode was then sandwiched in between two metallic lithium counter electrodes. The electrodes stack assembly was then wrapped around with a solvent-resistant adhesive tape so that the position of the electrodes remained in place. The two counter electrode tabs were spot-welded. The resistance between the counter electrode and the working electrode was measured to insure that the stack was not electronically shorted. The stack assembly was then placed in between three-layer white plastic packaging material (Shield Pack, Inc.) and sealed first three sides of the stack except the opposite end of electrode tabs. The sealed stack was then vacuumed and filled with a measured amount of 1M $LiPF_6$ electrolyte in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v) obtained from Grant Chemicals. The other end of the cell was then sealed. All these operations were carried out in a glove box (H_2O <1 ppm). The seal of the plastic bag was checked several times prior to taken out from the glove box for electrochemical measurements.

ii. Lithium-ion Cells

Prismatic design lithium-ion pouch cells were made with $LiCoO_2$ cathode and carbon fiber anode in 1M $LiPF_6$ electrolyte in EC/DMC (1:1 v/v). Figure 4 shows the pouch cell design. The cell configuration was as follows:

One-sided cathode (C/2)/Separator (S)/Carbon Fiber anode (A)/Separator (S)/One-sided cathode (C/2)

The fabrication procedure of the lithium-ion pouch cells was the same as that of half-cells as described above. A prototype lithium-ion pouch cell of capacity 500 mAh is shown in Fig. 5.

F. Electrochemical Measurements

i. Half-cells

The electrochemical measurements of the half-cells were carried out using an Arbin 24-channel cycler. The half-cells were first discharged at a constant current of 0.5 mA cm^{-2} to 0.005 V and then at a constant voltage (0.005 V) until residual current dropped to 0.05mA cm^2. The cells were then charged at a constant current of 0.5 mA cm^{-2} to a cut-off voltage of 1.0 V. The half-cells were discharged and charged for several times until a fairly constant value of charge capacity was obtained. The difference between the first discharge capacity and charge capacity provides the information on irreversible capacity loss of the working electrode (carbon fiber electrode).

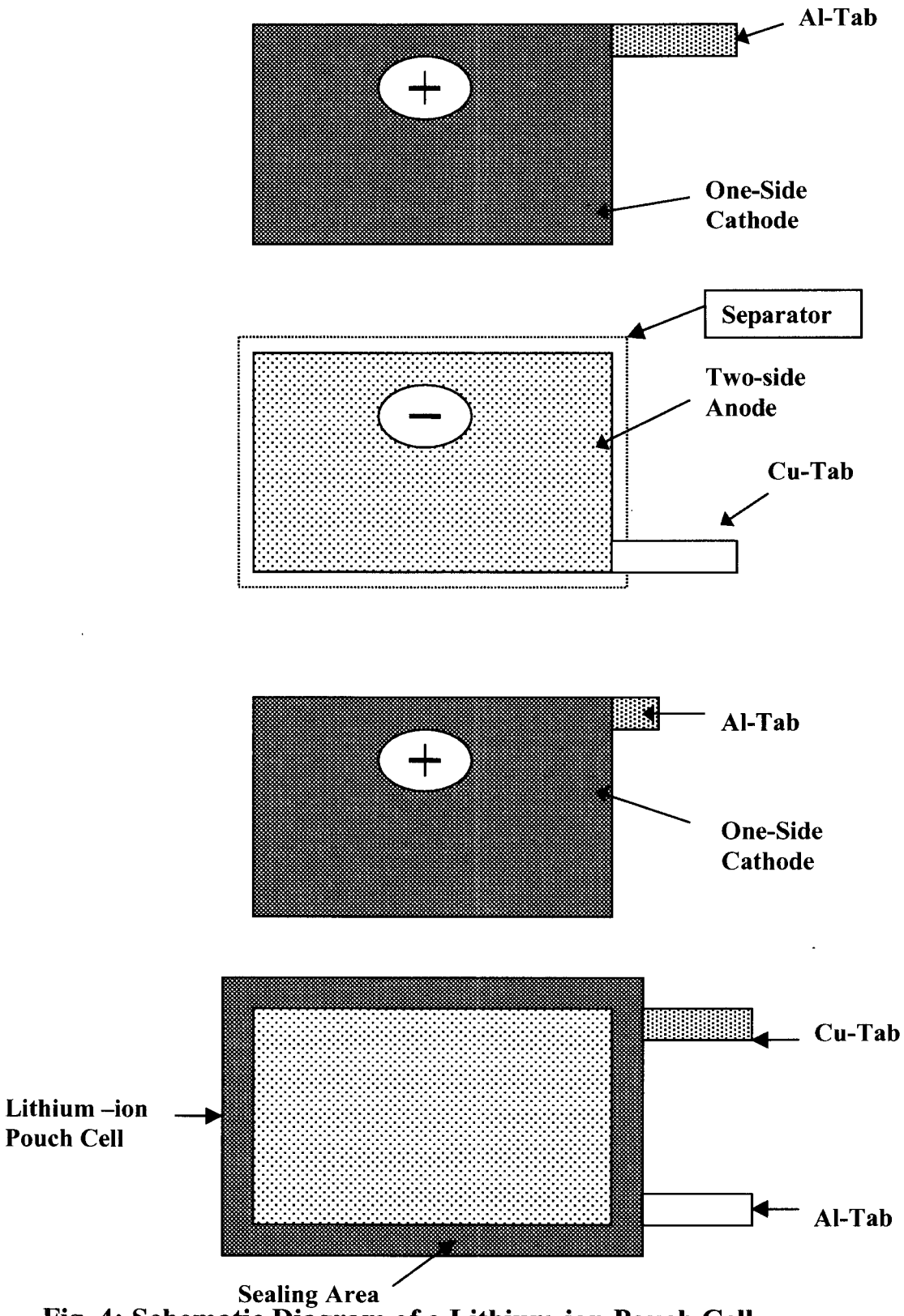


Fig. 4: Schematic Diagram of a Lithium-ion Pouch Cell.

ii. Lithium-ion Cell

The lithium-ion pouch cells were "formed" according to the following procedure:

The cells were first charged at a constant current of 0.5 mA cm^{-2} to 4.2 V and then at a

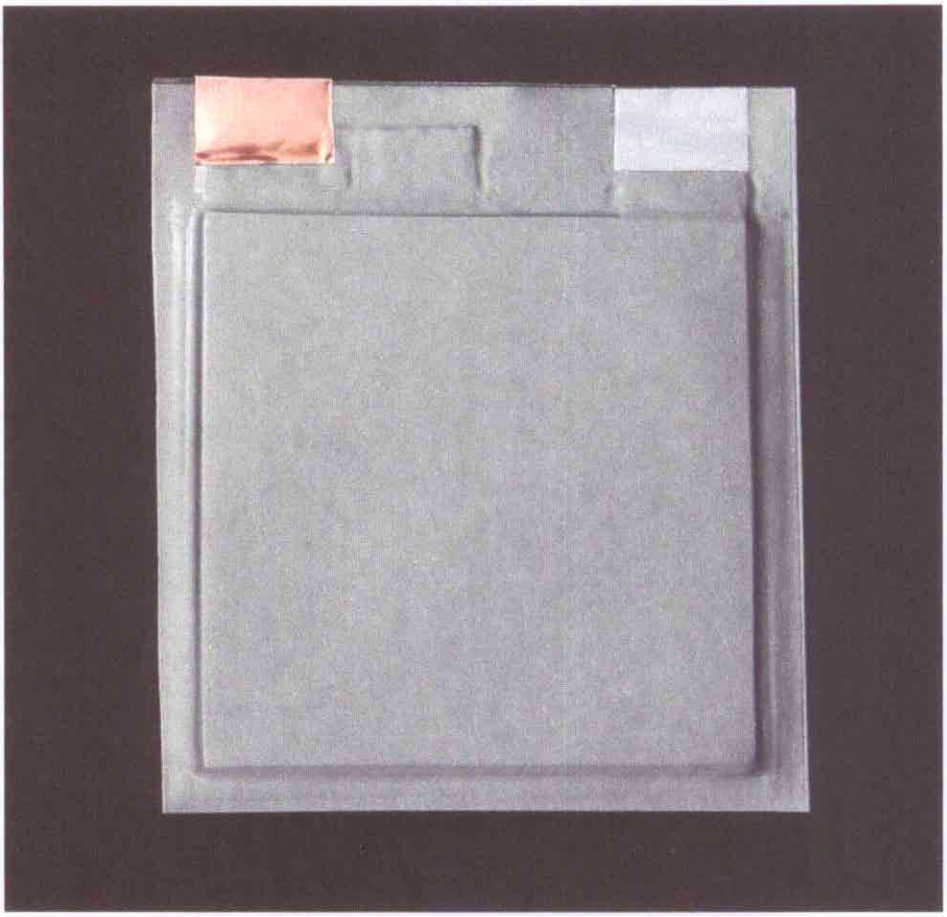


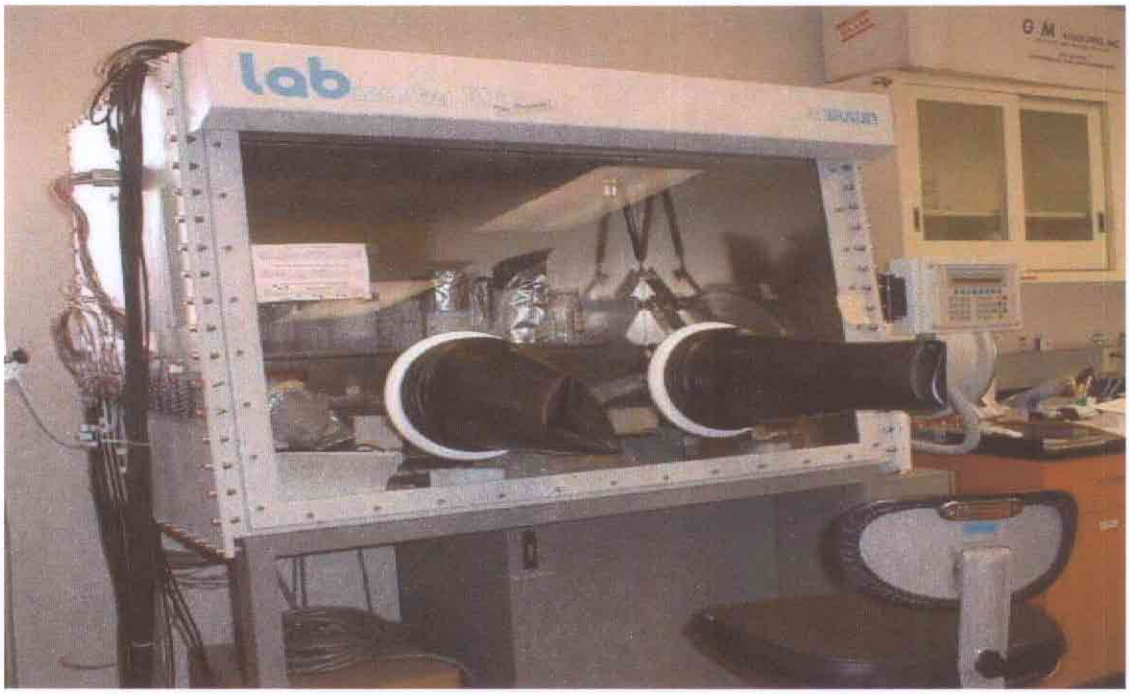
Fig. 5: A Prototype Lithium-ion Cell

Cell constant voltage (4.2 V) for a total period of 8 hours or until the current dropped to a value of 0.05 mA cm^{-2}. The cells were then discharged at a constant current of 0.5 mA cm^{-2} to a cut-off voltage of 2.5 V. The charge-discharge process was continued for several (usually 2-5) times until a fairly constant values of charge-discharge capacities were obtained. The "formed" cells were then used for performance evaluation. The difference between the first charge capacity and discharge capacity also provides the information on irreversible capacity loss of the lithium-ion cell.

MER's 24 Channel Battery Cycler

MER's 8 Channel GSM Battery Cycler

MER's Battery Testing Environmental Chamber



MER's Glove Box

IV RESULTS AND DISCUSSION

A. Half-cell Studies

i. Chopped Fiber-based Composite Electrode

The carbon-carbon (C-C) composite made from low cost chopped fiber and heat-treated to 3000°C was used to examine the behavior of lithium-ion insertion and removal during charge-discharge, respectively, in a half-cell measurement. The charge-discharge profile provides indication of reversibility and specific capacity of the composite for lithium-ion insertion/de-insertion.

Several half-cells were developed with the composite working electrode, lithium metal counter electrode, and 1M $LiPF_6$ electrolyte in a mixture (1:1 v/v) of ethylene carbonate (EC) and dimethyl carbonate (DMC) organic solvents. The composite of two different thickness (0.21 mm and 0.26 mm) was used for this investigation.

Figures 6 and 7 show the discharge-charge behavior of two representative half-cells made with the composite electrodes of 0.21 mm and 0.26 mm thick, respectively. The cells were first discharged at a current density of 0.6 mA/cm^2 to 0.0 V and then charged at the same rate to a cut-off voltage of 1.0 V. The cell with the thinner electrode delivered a specific capacity of 242 mAh/g whereas with the thicker electrode cell, a specific capacity of only 212 mAh/g was obtained. The lithium-ions transport to the composite electrode and diffusion of these ions to the electrode structure play significant role in delivering the specific capacity. The relatively thinner electrode is, therefore, critical in obtaining higher specific capacity. In commercial lithium-ion battery, a carbon electrode

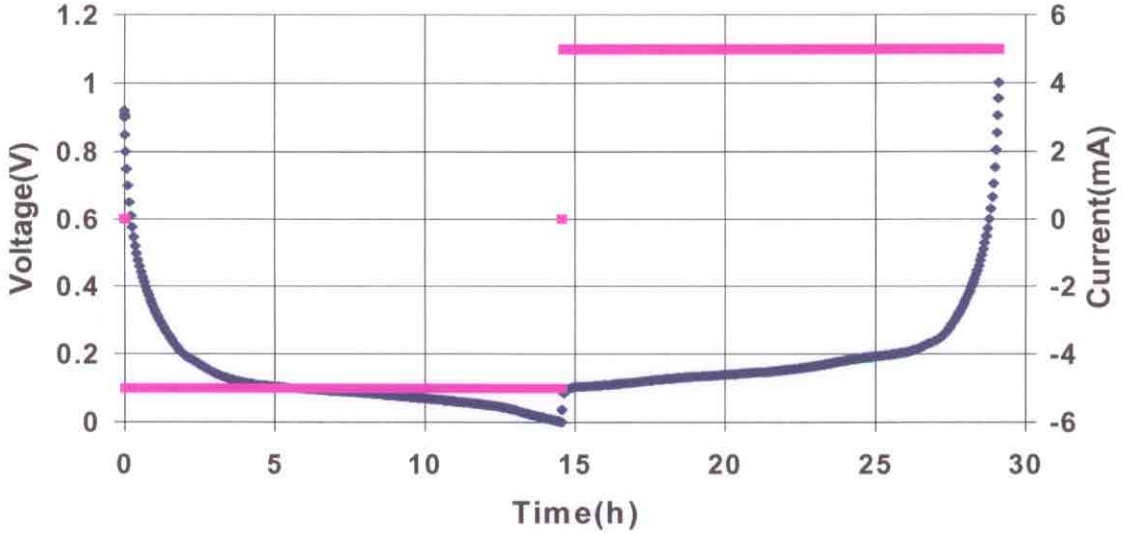


Fig. 6: Lithium-ion Intercalation/De-intercalation Behavior of C-C Composite made from Chopped Fiber. Counter Electrode: Li. Electrolyte: 1M $LiPF_6$ in EC/DMC (1:1 v/v).

of 0.15 mm thick is usually used which delivers a specific capacity of 330-340 mAh/g. Our focus will, therefore, be to produce C-C composite of approximately 0.15 mm thick using low cost chopped fiber.

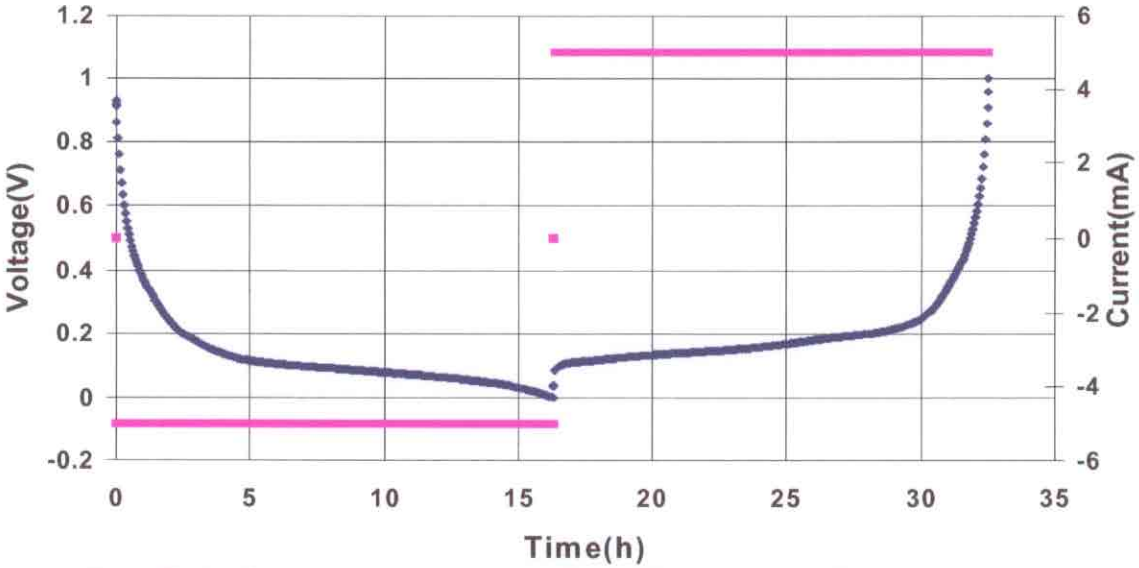


Fig. 7: Lithium-ion Intercalation (Discharge)/De-intercalation (Charge) Behavior of C-C Composite in 1M $LiPF_6$ Electrolyte (EC/DMC).

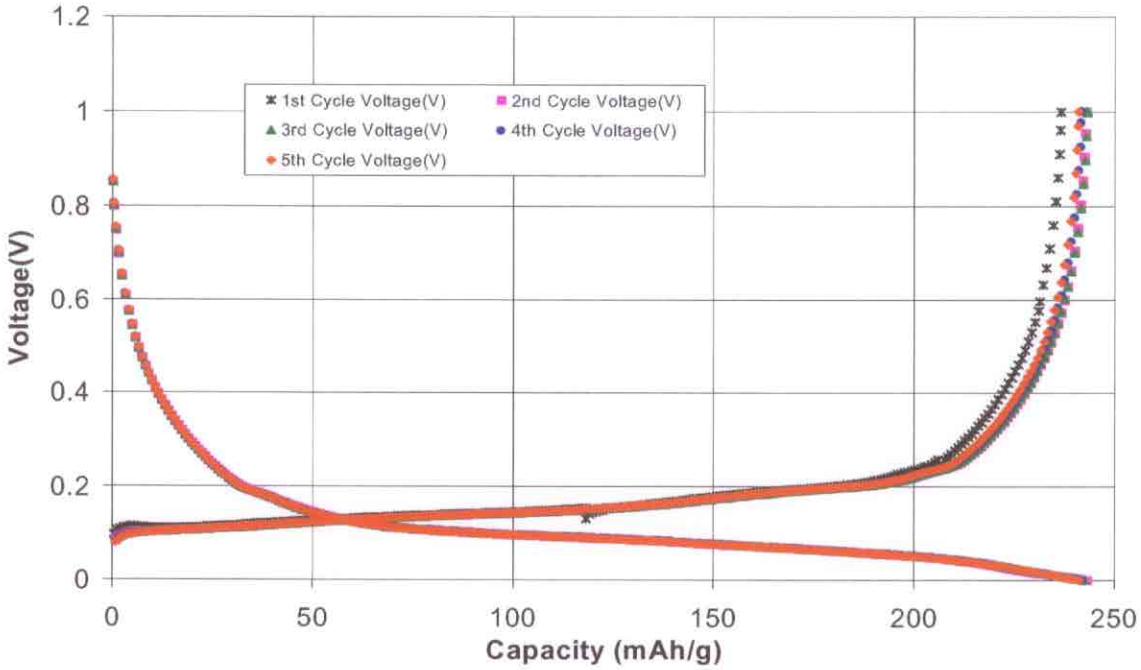


Fig. 8: Cycling Behavior of C-C Composite in 1M $LiPF_6$ (in EC/DMC 1:1 v/v) Electrolyte. Counter Electrode: Li.

The cyclability of C-C composite material has also been examined. Figures 8 and 9 represent the cycling behavior of two half-cells made with the C-C composite electrode of thickness 0.21 mm and 0.26 mm, respectively. Both the cells show excellent cycling behavior.

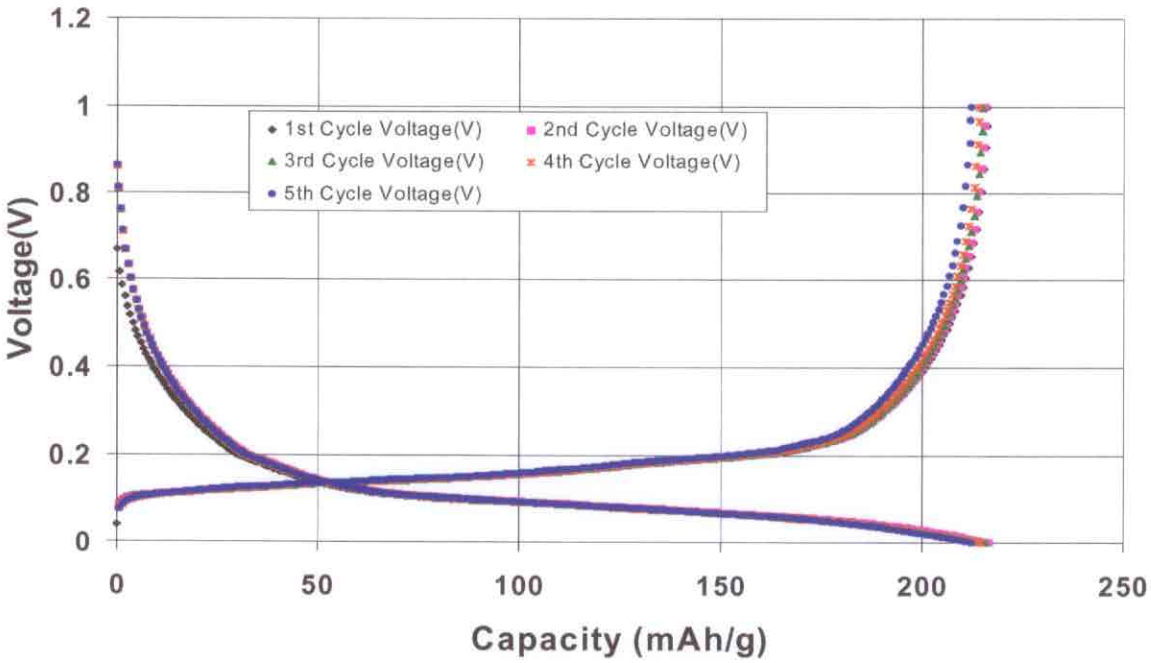


Fig. 9: Cycling Behavior of C-C Composite in 1M $LiPF_6$ Electrolyte (EC/DMC 1:1 v/v). Counter Electrode: Li.

We then focused on to processing to fabricate relatively thinner C-C composite (160 μm or less) using low cost chopped fiber, heat treat to ~3000°C, and testing the composite electrode for the intercalation/de-intercalation of lithium-ion in it.

Carbon-carbon (C-C) composite of 110 μm thick was made from low cost chopped fiber using the procedure outlined above and heat-treated to 2600°C. Several half-cells were developed with the composite working electrode, lithium metal counter electrode, and

1M $LiPF_6$ electrolyte in a mixture (1:1 v/v) of ethylene carbonate (EC) and dimethyl carbonate (DMC) organic solvents. The half-cells were then tested using Arbin 24 channel cycler which is equipped with a computer to monitor and store data.

Figures 10 shows the first discharge-charge behavior of a representative half-cell made with the composite electrode. The cell was first discharged at a constant current density of 0.6 mA/cm^2 to 0.0 V and then charged at the same rate to a cut-off voltage of 1.0 V. The first discharge capacity was 306 mAh/g and the corresponding charge capacity was 284 mAh/g. The irreversible capacity loss was, therefore, only 7% which is better than the best known commercial carbon material (MCMB ~10%).

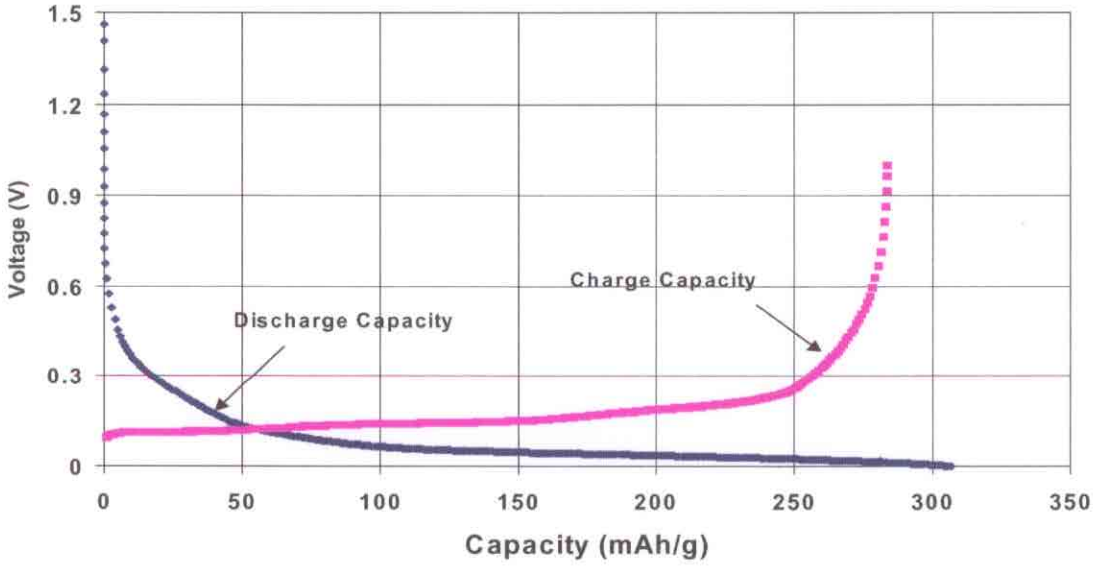


Fig. 10: First Discharge Charge Behavior of C-C Composite at 0.6 mA/cm^2 in 1M $LiPF_6$ Electrolyte.

The deliverable lithium-ion intercalation capacity is still significantly lower than that of commercial carbon. The primary reason for this is due to the relatively higher impedance of the C-C composite electrode as is evidenced from the sharp rise in voltage at open-

circuit voltage after charge. The iR drop due to this impedance has not been compensated during electrochemical measurements and thus results in lower deliverable capacity.

ii. Continuous Fiber-based Composite Electrode

We examined the charge discharge and cycling behavior of a thin (~50μm) C-C composite material, produced from P30X pitch-based carbon fiber and heat-treated to 2700°C, as anode in half-cell configuration. Metallic lithium was used as the counter electrode for half-cell studies in 1M $LiPF_6$ electrolyte.

Two half-cells were made. The electrode dimension was 2.5 cm x 3.5 cm. The open-circuit voltage of the cells were 3.31 V and 3.29 V. Both the cells were first discharged at a constant current of 0.5 mA/cm^2 to 0.0 V and then at constant voltage (0.0 V) for three hours or until the residual current dropped to 0.05 mA/cm^2. The cells were then charged at a constant current of 0.5 mA/cm^2 to a cut-off voltage of 1.0 V. Figure 11 shows the first charge discharge profile of a representative half-cell.

The cell delivered a first discharge capacity of 331 mAh/g and charge capacity of 305 mAh/g. The irreversible capacity loss is, therefore, 8%. The half-cells were discharged and charged for several times until a fairly constant value of charge capacity was obtained. Figure 12 represents the first four charge profiles of the cell. A fairly constant charge capacity of 343 mAh/g was observed which is considered to be the reversible capacity of the C-C composite anode.

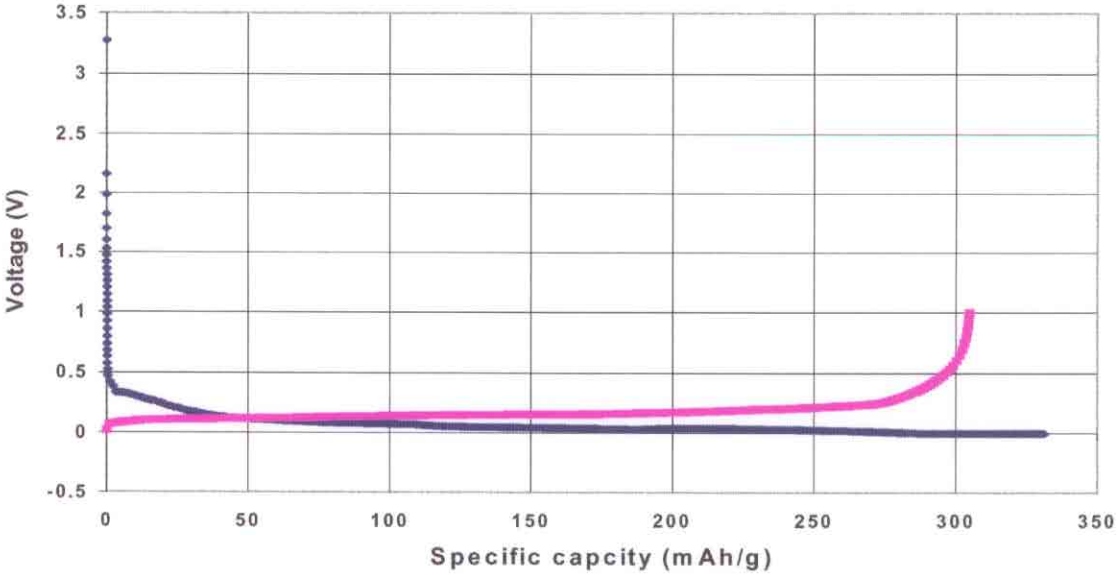


Fig. 11: First Discharge Charge Behavior of C-C Composite at 0.5 mA/cm2. Counter Electrode: Li; Electrolyte: 1M $LiPF_6$.

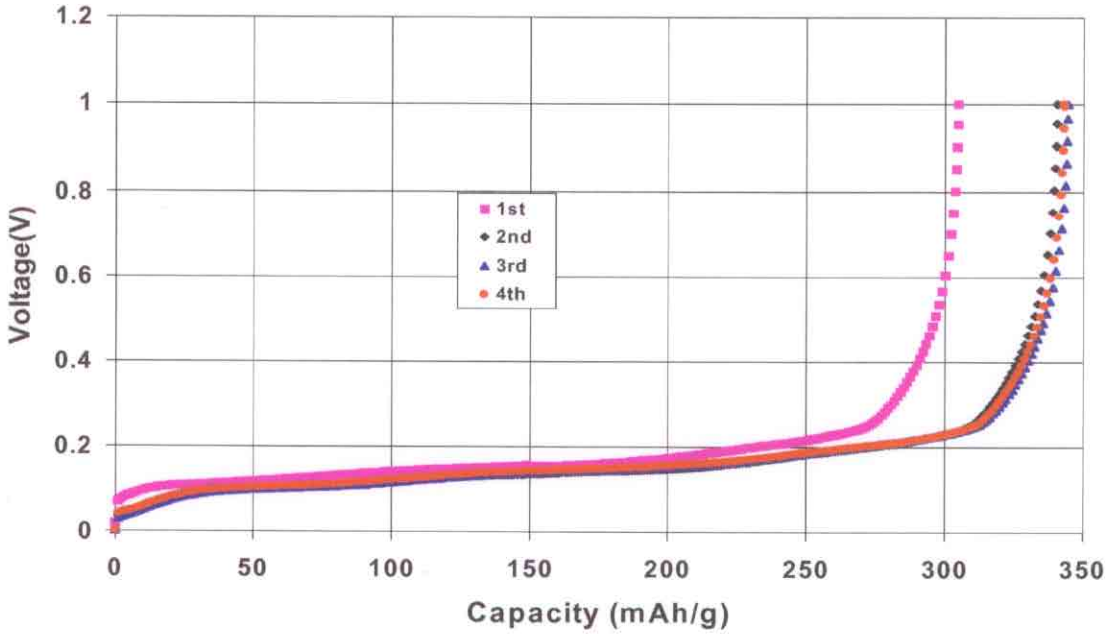


Fig. 12: Cycling Behavior of C-C Composite in 1M $LiPF_6$ Electrolyte. Counter Electrode: Li

Similar type of composite electrodes were made with P30X pitch-based carbon fiber but this time heat-treated to 2850°C The material was examined for lithium-ion intercalation and de-intercalation in 1M $LiPF_6$ electrolyte. Figure 13 shows the first discharge charge profiles. The charge capacity was 321 mAh/g with a corresponding discharge capacity of 336 mAh/g. An irreversible capacity loss of only 4% was observed. The irreversible capacity loss of 4% is significantly lower than that observed with MCMB carbon. The lower irreversible capacity loss improves specific energy and energy density of lithium-ion cells

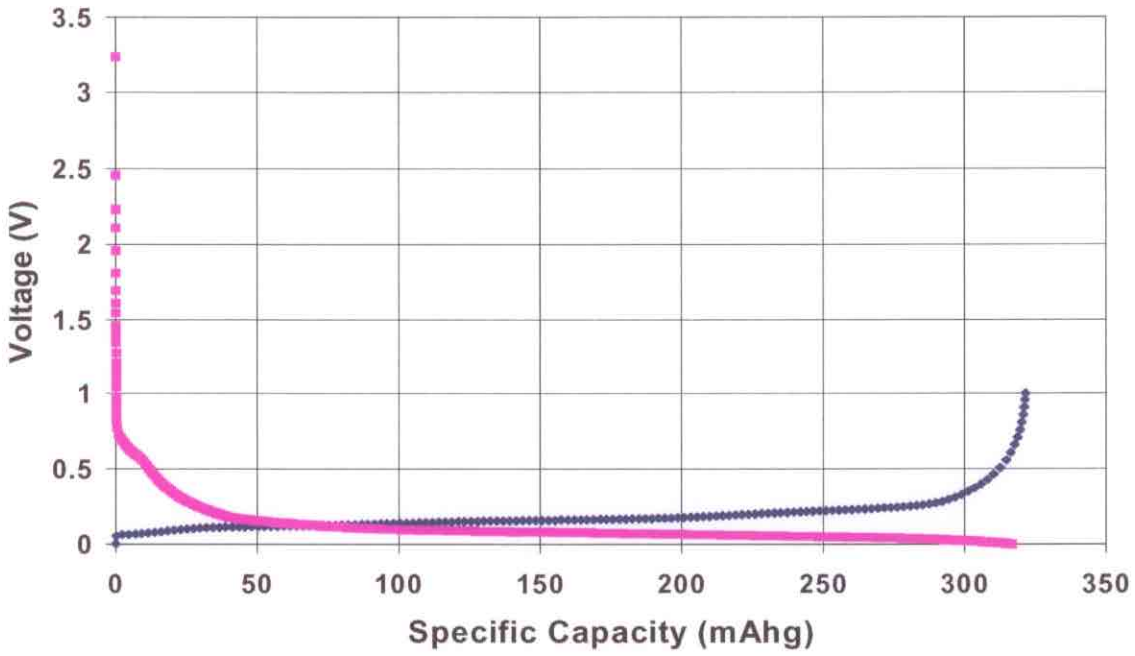


Fig. 13: First Discharge (intercalation) Charge (de-intercalation Behavior of C-C Composite in 1M $LiPF_6$ Electrolyte. Counter Electrode = Li

B. Lithium-ion Cell Studies

i. Chopped Fiber-based Composite Electrode

A number of prismatic design lithium-ion pouch cells were built with $LiNiCoO_2$ positive and C-C composite negative electrodes made from chopped carbon fiber and 1M $LiPF_6$ electrolyte in a mixture of ethylene carbonate and dimethyl carbonate.

The cells were first charged at a constant current of 60 mA to 4.2 V and then at a constant voltage (4.2 V) for a total period of 6 hours or until the current dropped to a value of 3 mA. The cells were then discharged at a constant current of 60 mA to a cut-off voltage of 2.5 V. The charge-discharge process was continued for several (usually 2-5) times until a fairly constant values of charge-discharge capacities were obtained.

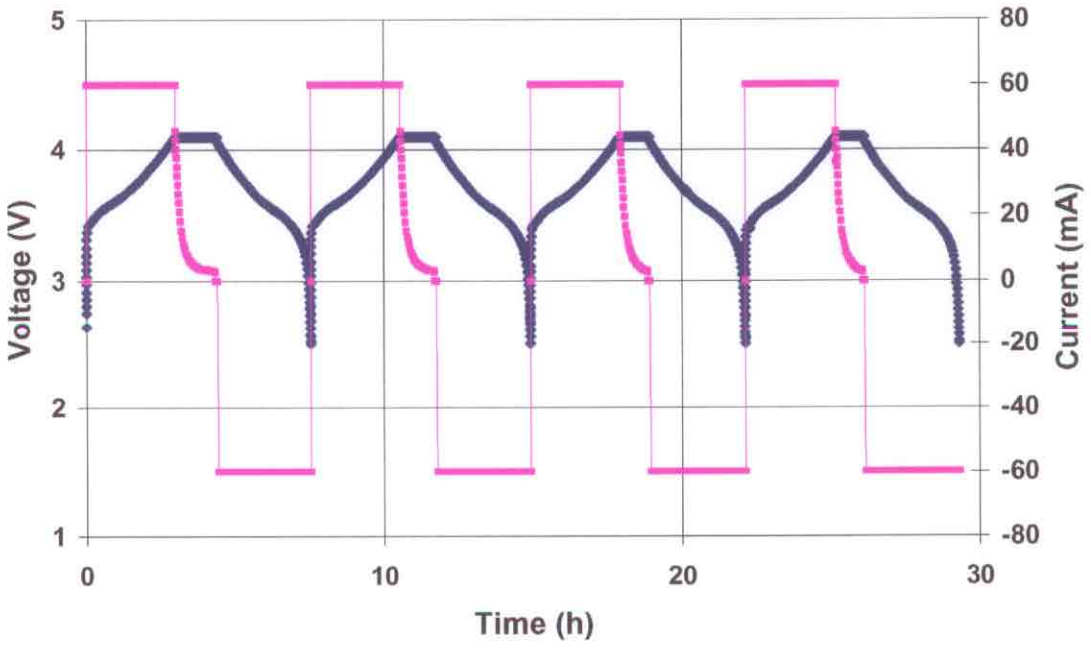


Fig. 14: Charge Discharge Behavior of a Prototype Prismatic Design Lithium-ion Pouch Cell.

The delivered capacities of the developed cells were determined at C/3 rate. Figure 14 shows the second to fifth cycles charge discharge profiles of a representative cell. During constant voltage charge, the residual current dropped to 2 mA sharply indicating very low impedance and no shorting of the cell. The charge capacities of the cell for the second to fifth cycles were 190.9 mAh, 190.9 mAh, 190.6 mAh, and 191.5 mAh and the corresponding discharge capacities were 188.5 mAh, 189.9 mAh, 192.6 mAh, and 190.5 mAh, respectively at 60 mA (C/3) current drain. The Coulombic efficiencies for the second to fifth cycles were 0.987, 0.995, 1.010, and 0.995, respectively.

ii. Continuous Fiber-based Composite Electrode

A number of prismatic design lithium-ion pouch cells were built with $LiNiCoO_2$ positive and C-C composite negative electrodes and 1M $LiPF_6$ electrolyte in a mixture of ethylene carbonate and dimethyl carbonate.

The cells were first charged at a constant current of 2 mA to 4.2 V and then at a constant voltage (4.2 V) for a total period of 6 hours or until the current dropped to a value of 0.2 mA. The cells were then discharged at a constant current of 2 mA to a cut-off voltage of 2.5 V. The charge-discharge profiles of two representative lithium-ion cells are shown in Fig. 15. The sharp fall of residual current indicates very low ESR of the cells.

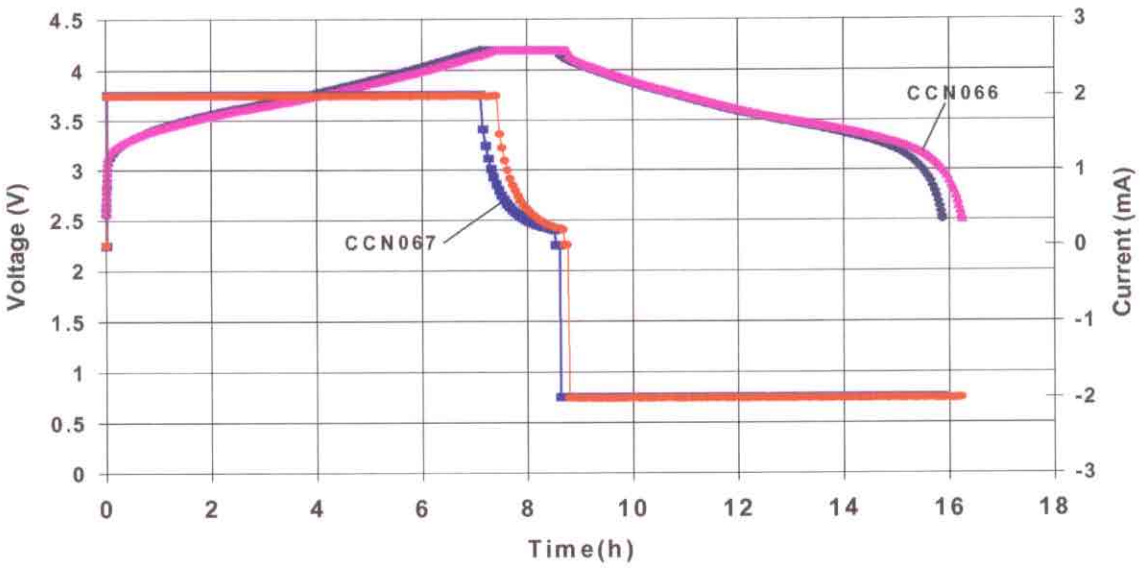


Fig. 15: Charge-Discharge Behavior of Li-Ion Cells made with C-C Composite Anode and $LiNiCoO_2$ Cathode in 1M $LiPF_6$ Electrolyte

Several prototype lithium-ion cells were cycled in the voltage regime of 2.5 V to 4.1 V. The cycling behavior of a representative cell is shown in Fig. 16 for 14 cycles. For clarity, the y-axis is shifted for charge and discharge cycles.

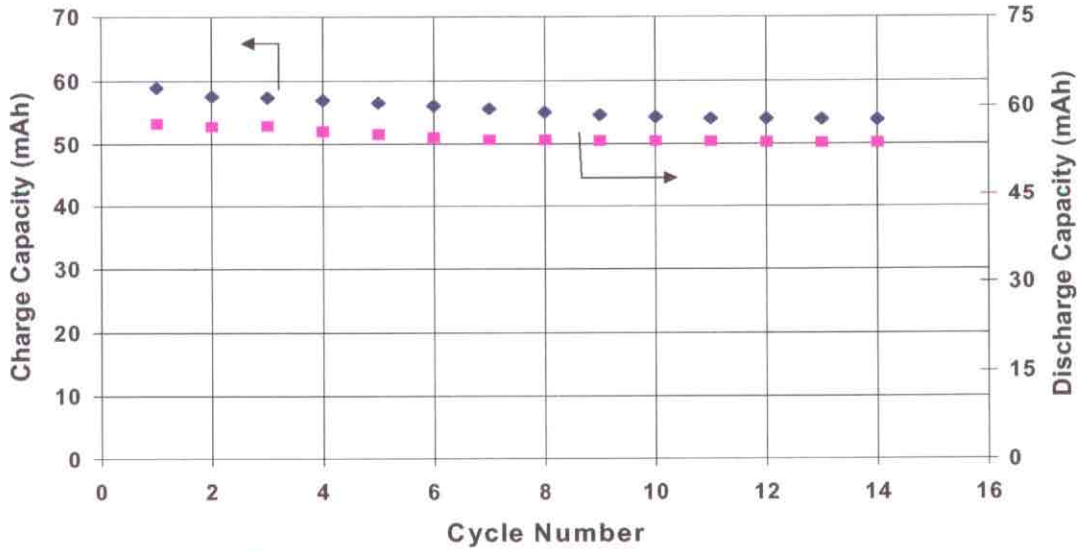


Fig. 16: Cycling Behavior of a Li-Ion Cell made C-C Composite Anode and $LiNiCoO_2$ Cathode in 1M $LiPF_6$. Discharge Rate: C/5.

After 14 cycles, the cell lost only 5% capacity.

The rate capabilities of the developed C-C composite-based lithium-ion cells have also been examined. Figure 17 shows the deliverable capacity of a representative cell at different discharge rates. The cell delivered almost 80% capacity at 2C rate.

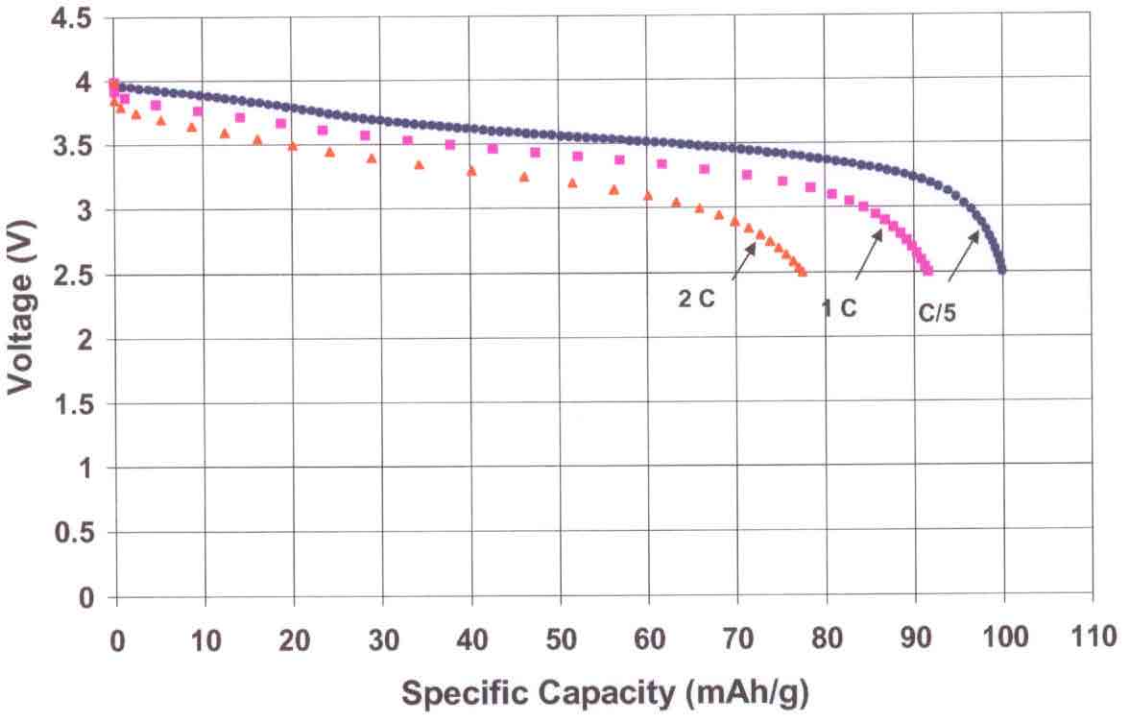


Fig. 17: Relative Capacity of a Li-ion Cell made C-C Composite and $LiNiCoO_2$ in 1M $LiPF_6$ Electrolyte

C. Preliminary Cost Analysis

These costs relate only to producing the carbon-carbon composite anode. Fabrication of lithium-ion batteries is well established no matter whatever the anode is.

The cost to produce C-C composites in general is also well established. For example, MER commercially produces C-C and depending on a variety of factors of part complexity, thickness of cross section, size, fiber type and heat treatment temperature, the sales prices is in the \$2.50 to \$7.00/in^3 range. Since a C-C composite for an anode,

depending on battery size, would be approximately 4 x 4 x 0.004 inches at 0.064 inches cube or at little less than 50 cents at the higher cost of $7.00/in^3. However, that cost is based on PAN based fiber and for the lithium-ion battery anodes, pitch based fiber and matrix is required.

The anodes produced in this year's investigation were Conoco discontinuous petroleum based pitch fibers and Amoco P30X continuous fibers. The Conoco fibers are at $10/lb and projected to go to under $5.00/lb. Coal tar pitch is used as the binder and its cost has been defined in another CPCPC program to produce fibers. Based on commercial coal tar pitch at $400/ton and the purification cost, the pitch binder cost is $0.4/lb, for a total cost of $0.6/lb.

The processing to produce the very thin anodes is a bit more complex than standard C-C processing, but in general follows the same processing steps as described above. The estimated processing cost per pound is $1.00.

The estimated cost for anode fabrication based on a 4 x 4 x0.004 inch anode which weighs approximately 0.0035 lb is as follows:

Item	**Cost/lb in $**
Pitch	0.20
Fiber	5.00
Processing	1.60
Total Cost	**$6.80**

This cost is within the projected precision of the $7.00/in^3 and produces commercial composites that suggest the anode cost per cell size of 4 x 4 inches is under 50 cents. It is clear the costs are projected at being quite low and substantially below the use of MCMB's, the standard available only from Japan.

The cost of using coal based pitch fiber in the future is estimated as about the same as the petroleum base pitch fiber from Conoco, that will result in a totally coal based anode with superior performance as an anode in lithium-ion batteries.

V. CONCLUSIONS

The primary objective of this Phase I program was to:

- Develop low cost, carbon fiber as anode materials for lithium-ion batteries, and
- Demonstrate their performance in half-cells and prototype lithium-ion cells configuration.

Our program objectives are successfully met or exceeded. We have developed half-cells with chopped and continuous carbon fibers-based electrodes and evaluated their reversible capacity and irreversible capacity loss for lithium-ion intercalation and de-intercalation. Both types of carbon fiber offer excellent reversible capacity for lithium-ion intercalation/de-intercalation. The continuous fiber, however, provides better irreversible capacity loss

We also developed prototype lithium-ion pouch cells with the developed composite anode materials and evaluated their performance such as cycleability and rate capability.

The superior performances demonstrated with the developed anode materials led to the foundation of continuation of Phase II program for the development of low cost long life lithium-ion cells for transportation and other commercial and military applications.

VI. REFERENCES:

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4. R. Fong, U. Von Sacken, and J. R. Dahn, J. Electrochem. Soc., 2009, **137,** 1990.

VII. LIST OF ACRONYMS AND ABBREVIATIONS:

C-C – Carbon-Carbon
CTP – Coal Tar Pitch
DEC – Diethyl Carbonate
DMC – Dimethyl Carbonate
DMF – Dimethyl Formamide
EC – Ethylene Carbonate
ESR – Equivalent Series Resistance
mAh – Milli Ampere Hour
MCMB – Mesocarbon Microbeads
NMP – N-Methyl Pyrrolidinone
PC – Propylene Carbonate
ppm – Parts per million
PVDF – Poly(vinylidene Fluoride)
SEI – Solid Electrolyte Interface
SEM – Scanning Electron Microscopy
V – Volt
Wh – Watt hour
XRD – X-ray Diffraction