

Carbon–carbon composite as anodes for lithium-ion battery systems

Sohrab Hossain^{*}, Yousry Saleh, Raouf Loutfy

LiTech LLC, 7960 S. Kolb Road, Tucson, AZ 85706, USA

Abstract

Carbon–carbon (C–C) composite has been investigated as an anode for lithium-ion battery systems. The composite electrode delivers high reversible capacity and very low irreversible capacity loss. The test results of lithium-ion cells made with the C–C composite anode show many advantages, such as excellent performance and enhanced safety. The performance improvement is achieved because of strong mechanical integrity (cycle life) and absence of binder (shelf life) in C–C composite. The enhancement in safety comes from high thermal conductivity, fire retardant characteristics and an acceptable ability to overcharge and overdischarge. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-ion batteries; Carbon–carbon composites

1. Introduction

The lithium-ion battery is considered to be the rechargeable battery of the future — from portable electronics, to aerospace and to vehicular applications. It provides high specific energy and energy density, excellent cycle life, low self-discharge and does not have memory effects. Because of its advantageous characteristics, lithium-ion batteries are widely used in portable electronic devices and are taking larger market shares each year from its competing technologies of Ni/Cd and Ni/MH. It has been forecast [1] that by the year 2003 most of the mobile consumer electronics will use lithium-ion batteries as their power sources.

However, the state-of-the-art lithium-ion battery system operates within certain voltage limits, beyond which either performance deteriorates and/or safety incidents, such as explosion/fire occur (see Fig. 1). The present lithium-ion battery system is, therefore, an almost zero tolerance technology. As such, overcharge and overdischarge protection circuits and/or devices are used in commercial lithium-ion batteries. For small, relatively low capacity, low voltage batteries, the above measures to protect the battery and users are found to be acceptable. For high capacity, multi-cell high voltage batteries, such as are being considered for use in aerospace and/or vehicular applications, an inherently safe battery chemistry is essential so that, if the battery experiences overcharge and/or overdischarge, there should not be any safety concerns.

The manufacturing of the state-of-the-art lithium-ion batteries demands high cost, sophisticated equipment for the production of cathodes and anodes of uniform loading. The relatively high capital investment and the use of overcharge/overdischarge protection circuits and/or devices are the main contributing factors to the high cost of lithium-ion batteries.

To address the above shortfalls, we have developed an anode based on carbon–carbon (C–C) composite material for lithium-ion batteries. The C–C composite offers many advantages, such as high reversible capacity and low irreversible capacity loss, excellent mechanical strength, good electrical and thermal conductivity, fire retardant characteristics and is reusable. It also offers an overcharge and overdischarge acceptance ability. This paper describes the intercalation/de-intercalation behavior of lithium-ions into the composite material and performance characteristics of lithium-ion cells made with the composite anode.

2. Experimental

2.1. Preparation of electrodes

2.1.1. The lithium electrode

The 3 μm thick expanded nickel mesh (Delker Corporation) was cut to the size of lithium electrode (25 mm \times 35 mm) 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 ($\text{H}_2\text{O} < 1 \text{ ppm}$) where 50 μm thick metallic

^{*} Corresponding author. Tel.: +1-520-574-1980.
E-mail address: shossain@merccorp.com (S. Hossain).

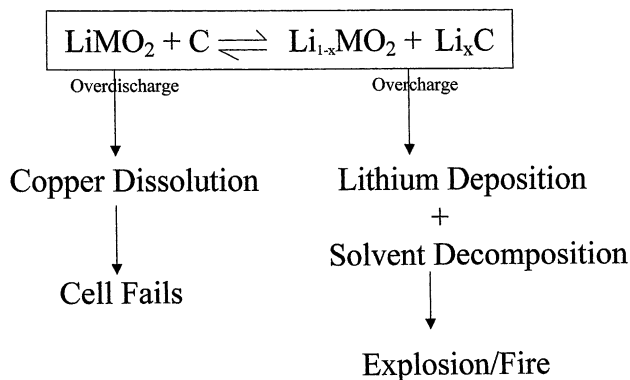


Fig. 1. Voltage limitation of present day lithium-ion battery technology.

lithium (Foote mineral) was press fitted to the substrates. These lithium electrodes were used as counter electrodes for half-cells measurements.

2.1.2. The C–C composite electrode

The C–C composite was obtained from MER Corporation. Some of the characteristics of C–C composite are shown in Table 1. The in-plane and cross-sectional views of the C–C composite are shown in Fig. 2(a) and (b), respectively. Fig. 3 shows a comparison of the X-ray diffraction patterns of the C–C composite with graphite. The C–C composite is composed of disordered carbon fiber. The composite plate was cut to the required dimensions (25 mm × 35 mm for half-cells and 50 mm × 62.5 mm to 130 mm × 190 mm for lithium-ion cells) and nickel foil was riveted to one edge of the plates. The resulting C–C electrodes with these nickel tabs were used as working electrodes for half-cells and anodes for lithium-ion cell studies.

Table 1

Characteristics of the C–C composite

Characteristics	Value
Surface area ($\text{m}^2 \text{g}^{-1}$)	0.19
Density (g ml^{-1})	1.6
Flexural strength (MPa)	45–50
Tensile strength (MPa)	155–160
Compressive strength (MPa)	45–50
Thermal conductivity (W mK^{-1})	550–650
Coefficient of thermal expansion ($\text{ppm } ^\circ\text{C}^{-1}$)	–1.7
Volume resistivity ($\mu\Omega \text{ cm}$)	250

2.1.3. The LiCoO₂ electrode

A slurry of 85% LiCoO₂ (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 a 40 μm thick aluminum substrate. The coated substrate was dried over hot air. It was then cut to the size of the positive electrodes (50 mm × 62.5 mm to 130 mm × 190 mm) with attached tabs for lithium-ion cells. The resulting positive electrodes were pressed, vacuum dried and stored in a desiccator prior to use.

3. Development of cells

3.1. Half-cells

Half-cells were made according to the following configuration: lithium electrode (Li)/separator (S)/C–C composite electrode (C)/separator (S)/lithium electrode (Li).

The C–C composite electrode was bagged using Celgard 2400 separator. The bagged working electrode was then

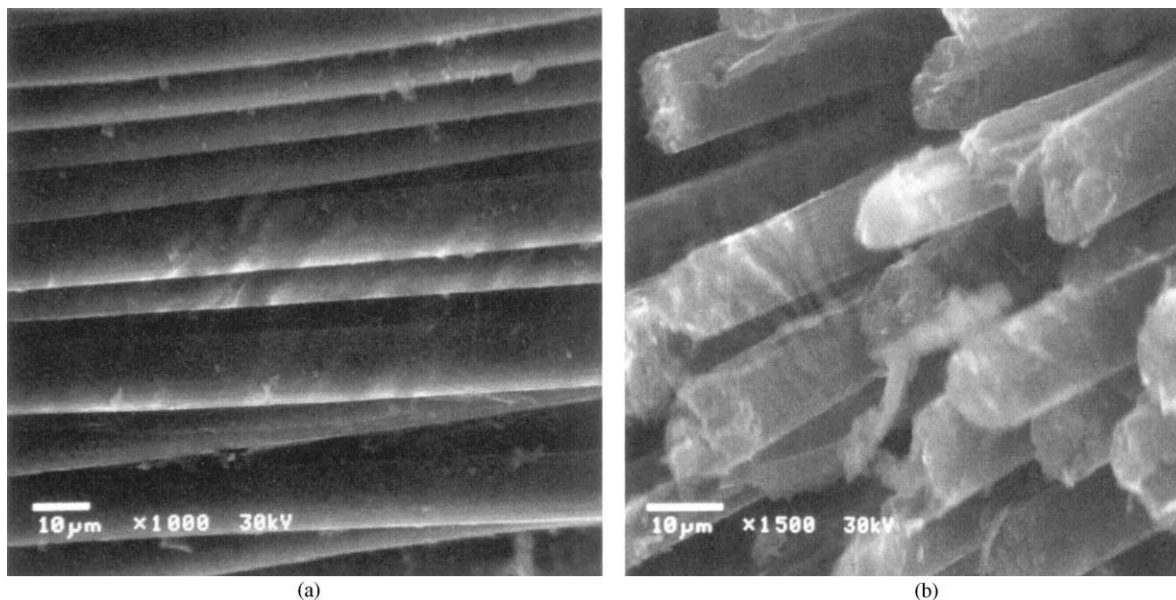


Fig. 2. SEM images of C–C composite (a) in-plane, (b) cross-section.

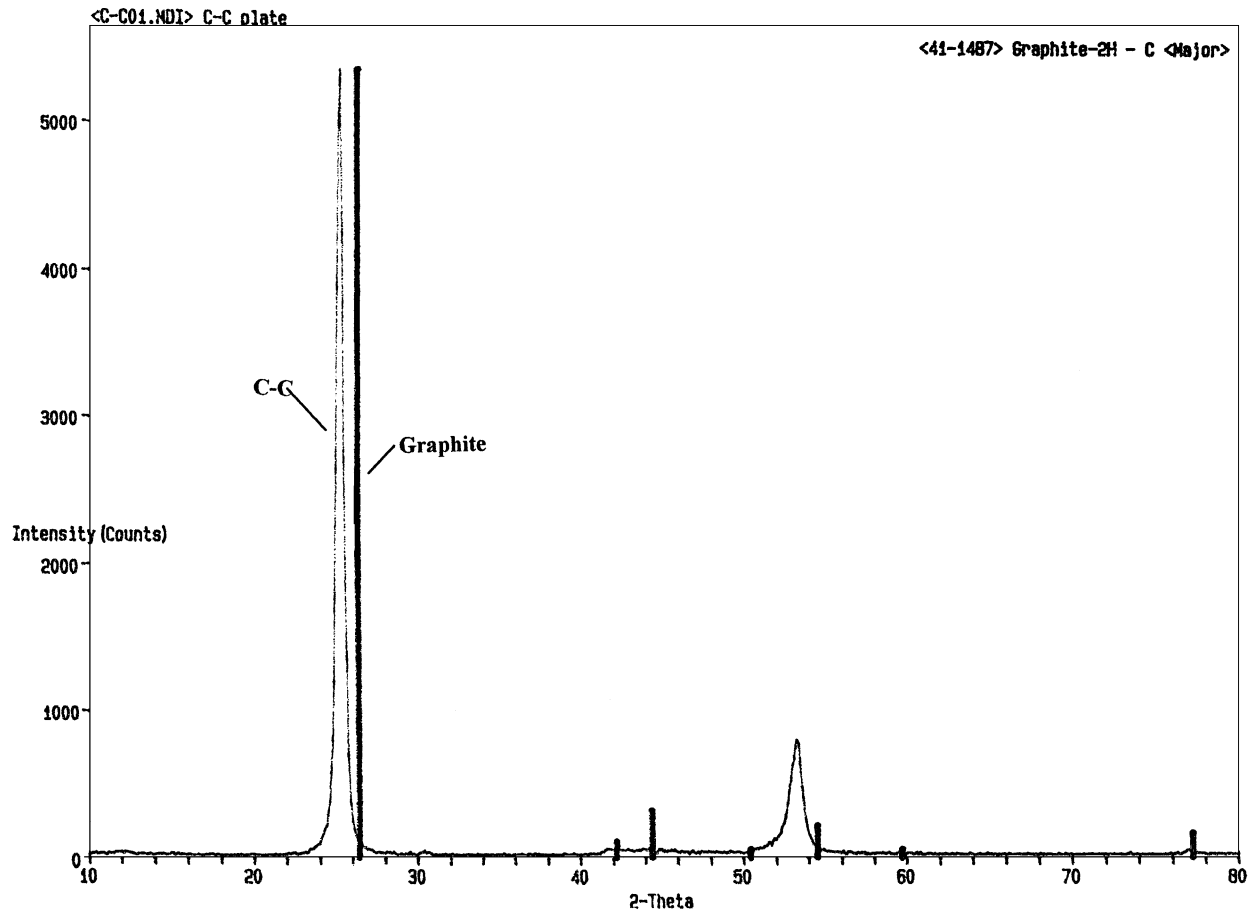


Fig. 3. X-ray diffraction patterns of C-C composite and of graphite.

sandwiched in between two metallic lithium counter electrodes. The electrode stack assembly 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 together. The resistance between the counter electrodes and the working electrode was measured to insure that the stack was not electronically shorted.

The stack assembly was then placed in between a three-layer white plastic packaging material (Shield Pack Inc.) and sealed along three edges of the stack leaving open the end opposite to the electrode tabs. The sealed stack was then vacuumed and filled with a measured amount of 1 M 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 ($\text{H}_2\text{O} < 1 \text{ ppm}$). The seal of the plastic bag was checked several times prior to taken out from the glove box for electrochemical measurements.

3.2. Complete lithium-ion cells

Prismatic lithium-ion pouch cells were made with two LiCoO_2 cathodes and a C-C composite anode in 1 M LiPF_6

electrolyte in EC/DMC (1:1 v/v). Fig. 4 shows the pouch cell design. The cell configuration was as follows: one-sided cathode (C/2)/separator (S)/C-C composite anode (A)/separator (S)/one-sided cathode (C/2).

The fabrication procedure of the lithium-ion pouch cells was the same as that of the half-cells described in clause 3.1. A prototype lithium-ion pouch cell of 1 Ah capacity is shown in Fig. 5.

4. Electrochemical measurements

4.1. On 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 0.05 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. 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

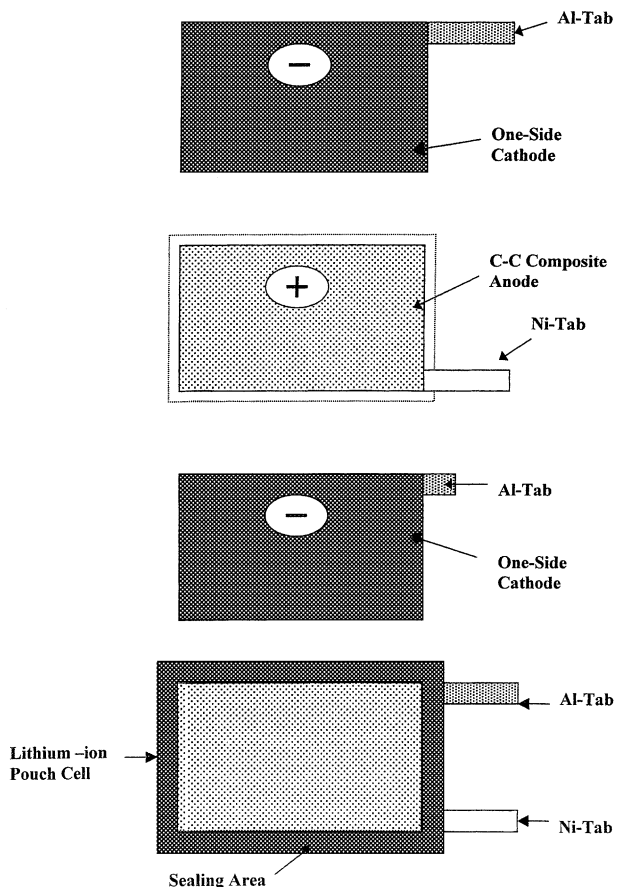


Fig. 4. Schematic diagram of a lithium-ion pouch cell based on C-C composite.

information on irreversible capacity loss of the C-C composite working electrode.

4.2. On lithium-ion cells

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 constant voltage (4.2 V) for a total period of 8 h 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 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.

5. Results and discussion

Several half-cells, made with C-C composite working electrode and lithium metal counter electrode, were used to investigate the intercalation and de-intercalation behavior of lithium-ions within the composite electrode. Based on the half-cell results, a number of lithium-ion pouch cells were built and their performance characteristics were evaluated. The results are discussed below.

5.1. Intercalation/de-intercalation of lithium ions

Fig. 6 shows a representative plot for the first discharge (intercalation) charge (de-intercalation) characteristics of

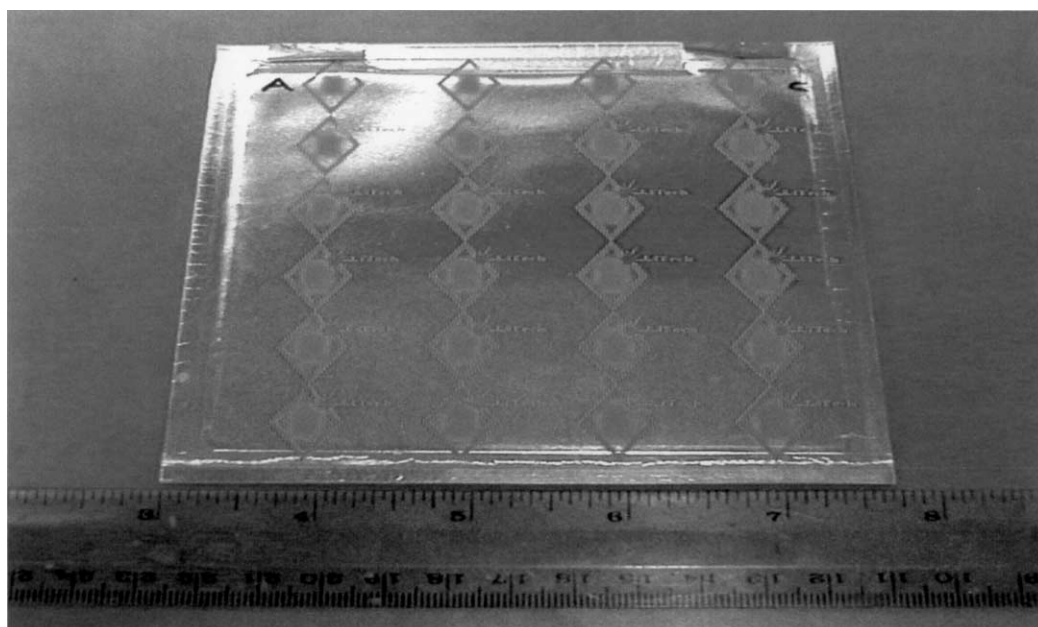


Fig. 5. Prototype 1 Ah lithium-ion pouch cell.

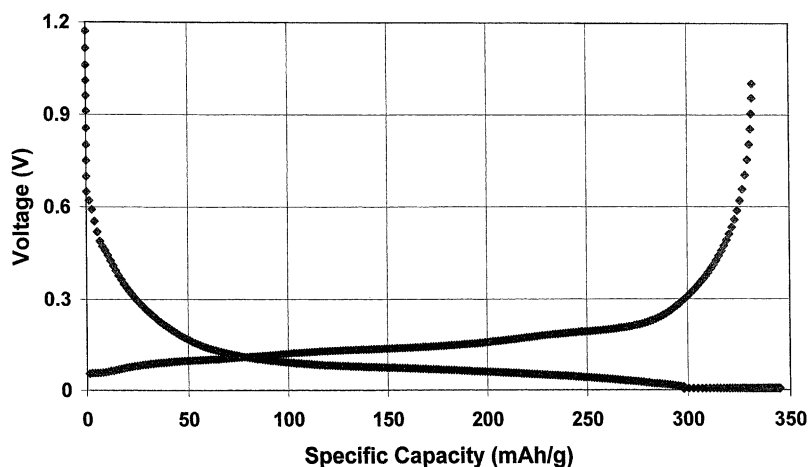


Fig. 6. Discharge-charge behavior of C-C composite at 0.5 mA cm^{-2} in 1 M LiPF_6 electrolyte (EC:DMC 1:1 v/v). Counter electrode: Li.

the C-C composite electrode against the lithium counter electrode. The first discharge and charge capacities due to lithium ions intercalation and de-intercalation correspond to 342 and 332 mAh g^{-1} of C-C composite, respectively. The irreversible capacity loss is, therefore, $<3\%$. This value of irreversible capacity loss is significantly lower than that obtained from the best commercial carbon (MCMB 2528) used by the lithium-ion battery industry. The low irreversible capacity loss is most probably related to the low surface area, absence of binder, carbon black and foreign materials, and little or no surface functional groups within the C-C composite.

The half-cell was cycled for four more times (see Fig. 7) to determine the specific reversible capacity and cycling efficiency of the C-C composite. An average reversible capacity of 335 mAh g^{-1} was obtained at 0.5 mA cm^{-2} with a Coulombic efficiency of 0.995 for the 2nd cycle, 0.994 for the 3rd cycle, 1.000 for the 4th cycle, and 0.998 for the 5th cycle, respectively. It is noteworthy to mention that the cell made with the C-C composite delivered a Coulom-

bic efficiency of more than 0.99 after completing only one discharge-charge cycle.

5.2. Overdischarge

Present state-of-the-art lithium-ion batteries need an overdischarge protection circuit. Overdischarge (discharge below 2.5 V) causes dissolution of the copper that is used as an anode substrate, and degrades cell performance.

One of the most important characteristics of C-C composite based lithium-ion cells is the ability to accept repeated overdischarge without performance deterioration. Fig. 8 represents a plot of repeated overdischarge. The cell was discharged at a constant current of 30 mA to -1.0 V . For the first two cycles, the cell was charged to 4.1 V and for the last two cycles, the charge voltage was 4.2 V . The capacities delivered during overdischarge are 180 , 179 , 193 , and 193 mAh for the cycles 1–4, respectively. In C-C composite based lithium-ion cell, C-C composite is the substrate and the active sites for electrochemical reaction.

5.3. Overcharge

Another important feature of C-C composite based lithium-ion battery technology is its tolerance of overcharge. Overcharge is one of the most important safety concerns of present state-of-the-art lithium-ion batteries. Overcharge causes metallic lithium to deposit on the anode, solvent decomposition, sharp rise in temperature, and ultimately thermal run away of the battery. To protect from overcharge, the lithium-ion battery industry uses a number of safety devices, such as overcharge protection circuits, positive temperature coefficient resistors, pressure sensitive rupture disks, temperature sensitive separators, etc.

Fig. 9 shows the voltage and temperature response of a fully charged cell (full capacity is 1 Ah) during overcharge at a constant current of 300 mA for 4 h followed by rest on open-circuit for 1 h . The temperature change recorded was

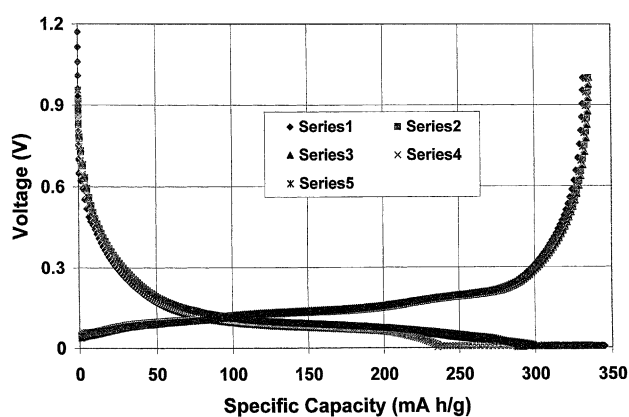


Fig. 7. First five discharge-charge curves of C-C composite at 0.5 mA cm^{-2} in 1 M LiPF_6 electrolyte (EC:DMC 1:1 v/v). Counter electrode: Li.

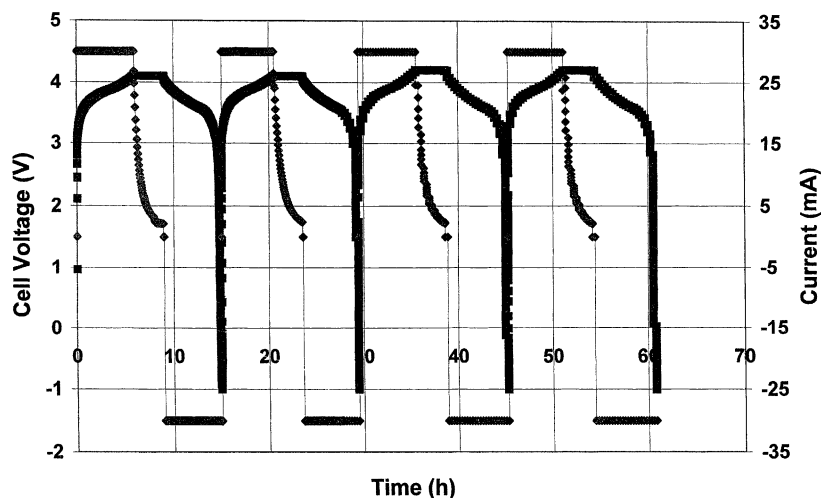


Fig. 8. Charge-overdischarge behavior of a lithium-ion cell based on C–C composite. Cathode: LiCoO_2 ; electrolyte: 1 M LiPF_6 in EC/DMC (1:1 v/v).

the outside body temperature of the cell. The voltage of the overcharged cell dropped sharply to about 4.7 V during rest period. During overcharge, the cell voltage went up monotonically to 4.8 V and then at a relatively higher rate to 5.7 V indicating that lithium-ion transfer was the dominant process initially, which was overtaken by the solvent decomposition after 4.8 V. There was an insignificant increase in cell temperature during overcharge.

5.4. Overcharge/overdischarge

Several lithium-ion cells made with the C–C composite anode were repeatedly overcharged and overdischarged. A representative plot is shown in Fig. 10. The cell was overcharged to 4.5 V and overdischarged to -1.0 V. The overcharged capacities were 240, 235, 235, and 235 mAh for

cycles 1–4, respectively. The corresponding overdischarge capacities were 230, 225, 225, and 225 mAh, respectively. The Coulombic efficiency under these overcharge/overdischarge conditions was 0.96.

5.5. Cycle life

The capacity fade of lithium-ion cells on cycling is mostly associated with the increase in impedance of electrodes. During the charge–discharge processes, expansion and contraction of the electrodes occur. The mechanical integrity of the electrodes plays an important role in minimizing the capacity fade.

The cycling behavior of a C–C composite based lithium-ion cell at 20°C is shown in Fig. 11. The cell was discharged at a constant current of $C/5$ and charged at the same constant

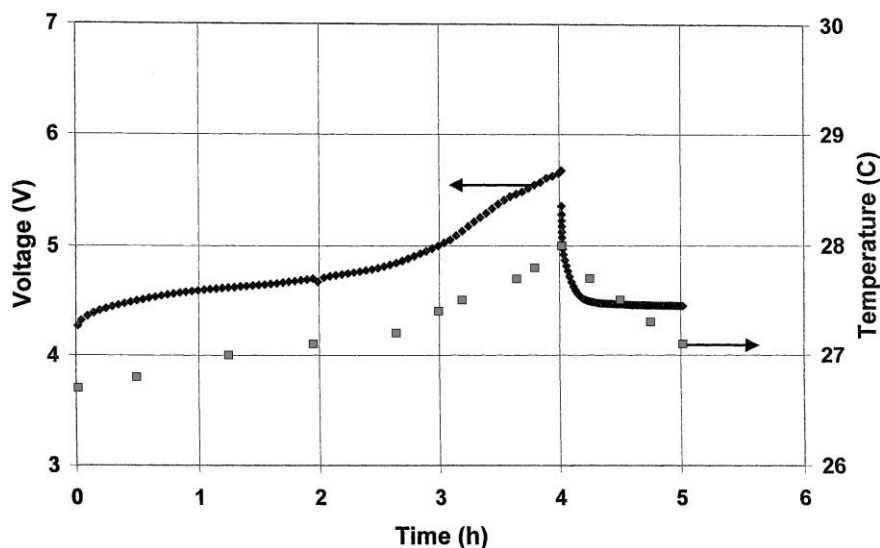


Fig. 9. Voltage and temperature responses during overcharge followed by open-circuit of an 1 Ah lithium-ion cell. Cathode: LiCoO_2 ; electrolyte: 1 M LiPF_6 in EC/DMC (1:1 v/v).

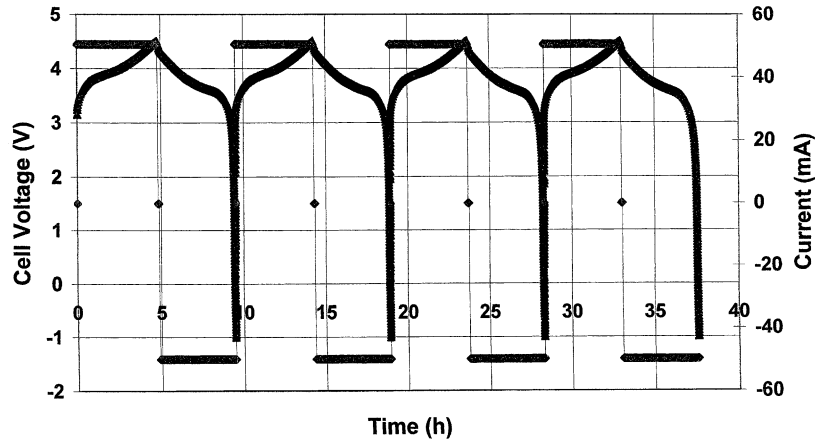


Fig. 10. Repeated overcharge–overdischarge behavior of a lithium-ion cell based on C–C composite. Cathode: LiCoO_2 ; electrolyte: 1 M LiPF_6 in EC/DMC (1:1 v/v).

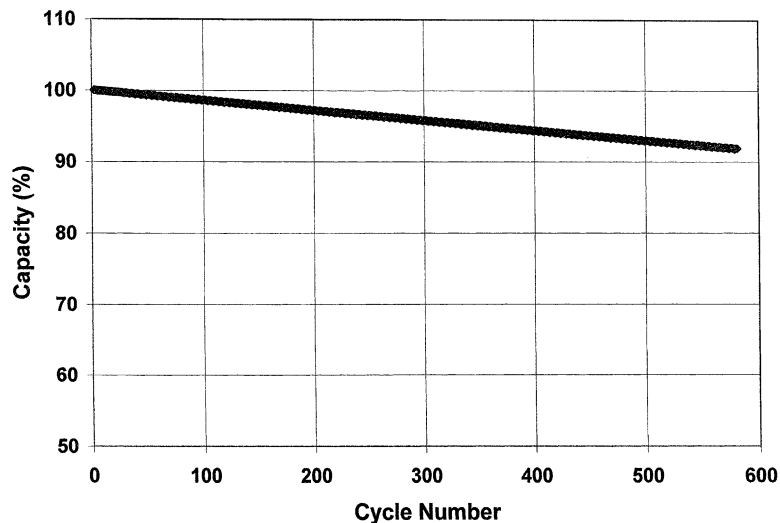


Fig. 11. Cycling behavior at C/5 rate of a lithium-ion cell based on C–C composite. Cathode: LiCoO_2 ; electrolyte: 1 M LiPF_6 in EC/DMC (1:1 v/v).

current rate to 4.2 V and then at constant voltage (4.2 V) for 3 h or until the residual current dropped to C/50. The cell delivered over 550 cycles with <10% capacity loss. The high cycle life is associated with the strong mechanical integrity of C–C composite electrode.

5.6. Self-discharge

The self-discharge characteristics of lithium-ion cells, made with C–C composite and also with commercially available MCMB 2528 graphite, were investigated at ambient temperature. After being fully charged, the cells were stored on open-circuit for 1 month (720 h), and the decay of voltage recorded. Fig. 12 compares the voltage decay of two representative cells. A voltage drop of only 10 mV was observed for C–C composite based cell whereas for MCMB 2528 based lithium-ion cell a voltage drop of 60 mV was observed after this 1 month of storage.

The stored cells were then discharged to compare the delivered capacity before and after storage. Fig. 13 shows the discharge characteristics and compares the self-discharge behavior of the cell made with C–C composite. The cell lost about 2% capacity after storage for 1 month. The cell with MCMB 2528 carbon shows about 8% capacity loss after storage for 1 month. The low self-discharge behavior of C–C composite based lithium-ion cell is probably related to the low surface area of C–C composite, absence of binder, carbon black and foreign materials, and relatively little or no surface functional groups.

5.7. Safety and abuse tests

A number of safety and abuse tests have been carried out on fully charged C–C composite based 1 Ah lithium-ion cells. The cells were cycled at least 50 times prior to the safety tests. The test results summarized in Table 2.

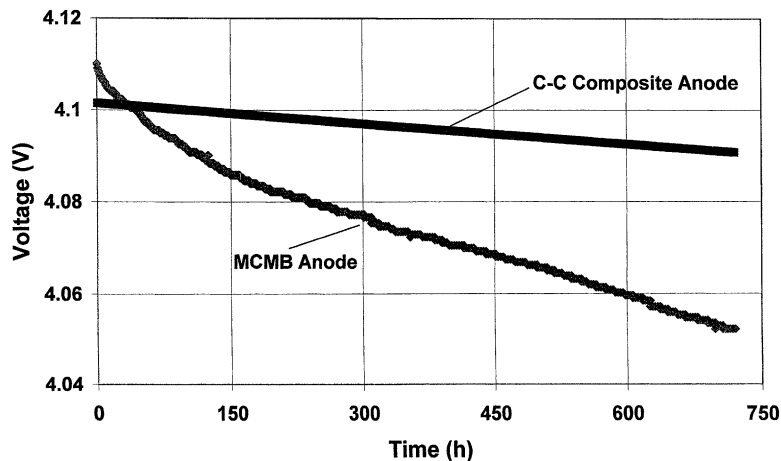


Fig. 12. Voltage decay of lithium-ion cells made with C–C composite and MCMB 2528 graphite stored on open-circuit at ambient temperatures. Cathode: LiCoO_2 ; electrolyte: 1 M LiPF_6 in EC/DMC (1:1 v/v).

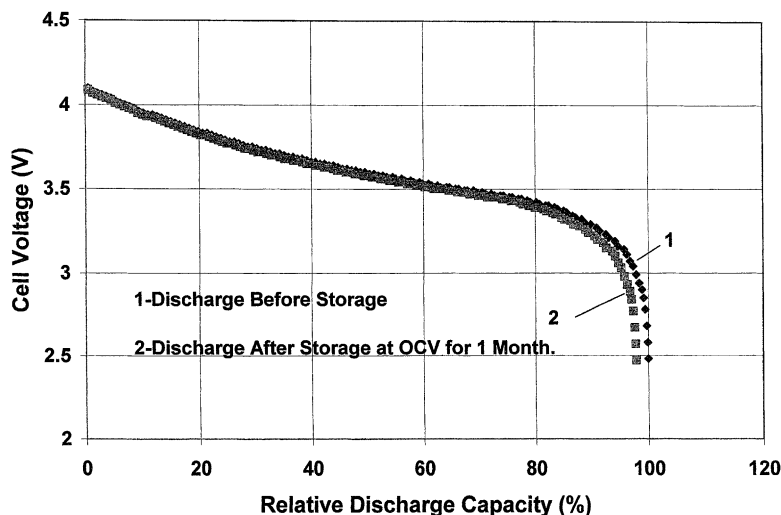


Fig. 13. Discharge behavior at C/4 rate of a lithium-ion cell based on C–C composite before and after storage for 1 month under ambient temperature. Cathode: LiCoO_2 ; electrolyte: 1 M LiPF_6 in EC/DMC (1:1 v/v).

The enhanced safety of C–C composite based lithium-ion cells is related to the fact that the composition of anode in a fully charged cell is LiC_{12} (substrate is C–C composite which is also available for lithium-ion intercalation). This compound is much less reactive than LiC_6 that is formed in the conventional graphite based lithium-ion cells. During overcharge, the anode composition of C–C composite based

cell becomes LiC_x , where x is <12 , but ≥ 6 . Also, there is no deposition of metallic lithium.

On the other hand, metallic lithium deposits on the graphite or carbon based anode of commercial lithium-ion cells if they are overcharged. So, the use of C–C composite as anodes for lithium-ion batteries allows extension both of performance and safety limit boundaries.

Table 2
Safety and abuse test results

Test	Results
Overdischarge	No performance degradation
Overcharge	No fumes, fire, or explosion
External short-circuit	No fumes, fire, or explosion
Internal short-circuit (nail penetration)	No fumes, fire, or explosion

6. Conclusion

Carbon–carbon (C–C) composite has been investigated as an anode for lithium-ion batteries. The C–C composite offers many advantages, such as:

- High reversible capacity and very low irreversible capacity loss.

- Anode substrate is carbon — no dissolution of substrate during overcharge.
- Substrate and lithium intercalation sites are indistinguishable — can act as lithium-ion sink during overcharge.
- In the charged state, lithium-ions are present as less reactive LiC_{12} rather than highly reactive LiC_6 .
- Strong mechanical integrity provides high cycle life.
- Low self-discharge associated with high compression, low surface area, and absence of binder, carbon black, and foreign materials.

- High thermal conductivity can provide ease of thermal management for high capacity, high voltage batteries.

The C–C composite can, therefore, be considered as a strong candidate for the anodes of lithium-ion batteries.

Reference

- [1] Power 2000, San Diego, CA, USA, 24–27 September 2000.