

# High energy Li-ion rechargeable battery using thin lithium film composite separator

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## Abstract

It has been demonstrated that small amounts of active lithium metal can be added to a lithium-ion (Li-ion) battery via the separator by using vacuum deposition techniques. Lithium films (4–8  $\mu\text{m}$ ) were deposited onto micro-porous polypropylene film that is used as the separator in Li-ion cells. We have demonstrated that the lithium electrochemically reacts with either electrode depending on the geometry of assembly. As a result, the intrinsic irreversible capacity of negative electrode can be compensated using volumetrically efficient lithium metal. Hence, Li-ion cells can be designed and constructed with significantly higher energy than those assembled with conventional techniques. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Li-ion battery; Irreversible capacity; Thin lithium film on separator

## 1. Introduction

The total energy that can be designed into batteries is dependent on the specific capacities, densities, and efficiencies of the electrode materials. For the highest capacity, cells are designed with nearly matching electrode capacities. Often, however, the electrode balance is deliberately mismatched for stability, overcharge protection or other reasons. This normally results in a penalty with regard to overall capacity of the battery.

In many rechargeable cell systems, and especially lithium-ion (Li-ion) battery, the efficiency (ratio of the first discharge to charge capacity) of the negative electrode is significantly different from that of the positive electrode [1–3]. It has been reported that Li ion reacts with organic electrolytes on the surface of carbon negative electrode, generating a solid electrolyte interface (SEI) [1,2]. Such reaction irreversibly consumes active lithium, resulting in an irreversible capacity loss after the first cycle. In practi-

cal cell designs, the irreversibility of the negative electrode is compensated for by using excess positive electrode material that contributes the needed active lithium ions. The large irreversibility of carbon negative electrode and moderate density of lithium metal oxide positive electrode, which is present in excess, consequently results in reduction of overall capacity and energy density of the Li-ion battery.

In order to achieve the most efficient design, it would be ideal to compensate the irreversible capacity of negative by means of adding high volumetrically efficient lithium metal as opposed to the volumetrically and gravimetrically inefficient lithiated metal oxides positive. Directly contacting a sheet of lithium metal to carbon negative electrode in Li-ion battery has been proposed by Fong et al. [4], but practical application requires that the lithium film is as thin as a few micrometers.

We report in this paper a novel process that deposits thin lithium layer on the separator to form a composite material. When incorporated into a cell, the composite material will react with the electrodes with which it is in contact with and compensate for excess capacity. As a result, the composite material allows higher capacity designs to be utilized [5].

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## 2. Experimental

### 2.1. Depositing Li on separator

The lithium deposition experiments were performed in a high vacuum ( $10^{-6}$  Torr) evaporator (Denton Vacuum DV-502) in a dry room. Lithium metal (0.05 g) was loaded in a small aluminum oxide crucible surrounded by a Tungsten basket heater (Kurt J. Lesker) that was connected to two electrodes at the center of a chamber. Polypropylene separator specimens were placed on a rotating plate (50 rpm) about 10 cm above the lithium source. The evaporation was carried out by a 20-mA (DC) operation current for 10 min, the deposition being confirmed by a shiny sliver-like deposit on the separator specimens. The specimens were then transferred to a glove box filled with argon gas. The total amount of lithium was determined from LiOH solution by ICP. The thickness of lithium deposit was calculated from total amount of lithium, total area of specimen, and the density of lithium. The typical thickness of lithium-deposited separator specimens was 4–8  $\mu\text{m}$ .

### 2.2. Li-ion coin cells assembling and test

Coin type Li-ion cells were made by assembling carbons negative, metal oxide positive and separator (2.85  $\text{cm}^2$  active area) in a sandwich manner with 1.0 M LiPF<sub>6</sub> in EC/DMC (1:1) electrolyte. Two configurations were used in constructing the cells with Li-coated separators, facing lithium to (1) positive (cathode, FTC) and (2) negative (anode, FTA), respectively. The cell balance between two electrodes was determined by the ratio of negative and positive capacities observed on the first charge of cell. The capacity of lithium on the separator was added to positive or negative for the FTC or FTA design, respectively. Table 1 summarizes the experiments and testing conditions in detail.

## 3. Results

### 3.1. MCMB / LiCoO<sub>2</sub> system without reduced cathode design

Trials 1 and 2 were conducted in a design that added about 16% extra capacity from 4  $\mu\text{m}$  thick Li film to lithium cobalt oxide positive (FTC configuration) to compensate the irreversible loss on MCMB negative (Table 1). Coin cells thus made were cycled by a constant current of 0.5 mA (0.2 mA/ $\text{cm}^2$ ) for 24 h including trickling between 4.2 and 2.8 V. Fig. 1(a) to (c) illustrates the voltage profiles of Li-ion cells with and without lithium compensation capacity at 1st, 2nd, and 5th charge and discharge cycles. At the first cycle, cell with Li deposit, as indicated in Fig. 1(a), shows a voltage plateau between 1.0 and 3.6 V during charge. Approximately 150 mV lower running voltage, on the other hand, was found during discharge. The positive discharge capacity at this cycle was 20 mA h/g lower than that of the control cell. These results suggest that the lithium film start reacting once cell was charged. It should be noted that the reaction seems to take a few cycles to be completed. At the second cycle, the voltage plateau no longer exists, the discharge capacity of positive material being the same as that of control cell (Fig. 1(b)). A slightly low running voltage (50 mV lower than control) was still found. After five cycles, as indicated in Fig. 1(c), the cell performed like the control cell. Both charge and discharge capacities, however, were 30% higher than those of control cell.

Table 2 compares the cyclability of both types of cells. It can be seen from the cycling data that the compensated capacity from lithium composite film contributes to an increase in the total capacity of cell after a few cycles. At the end of the 5th and 20th cycles, the discharge capacities of the positive were 130 and 118 mA h/g, compared to 100 and 86 mA h/g of control. More than 30% improvement in terms of positive capacity was obtained. The

Table 1  
Li-ion coin cells construction and balance

| Trials | Cell chemistry <sup>a</sup>         | N/P ratio <sup>b</sup> | Lithium film        | N/P ratio <sup>c</sup> | Cycling conditions    |
|--------|-------------------------------------|------------------------|---------------------|------------------------|-----------------------|
| 1      | MCMB/LiCoO <sub>2</sub>             | 1                      | No                  | 1                      | 4.2–2.8 V trickling   |
| 2      | MCMB/LiCoO <sub>2</sub>             | 1                      | 4 $\mu\text{m}$ FTC | 0.84                   | 4.2–2.8 V trickling   |
| 3      | PC/LiMn <sub>2</sub> O <sub>4</sub> | 1.1                    | No                  | 1.1                    | 4.3–2.8 V w/o trickle |
| 4      | PC/LiMn <sub>2</sub> O <sub>4</sub> | 1.4                    | 4 $\mu\text{m}$ FTC | 1.1                    | 4.3–2.8 V w/o trickle |
| 5      | PC/LiMn <sub>2</sub> O <sub>4</sub> | 1.4                    | 4 $\mu\text{m}$ FTA | 1.1                    | 4.3–2.8 V w/o trickle |
| 6      | PC/LiMn <sub>2</sub> O <sub>4</sub> | 1.7                    | 8 $\mu\text{m}$ FTC | 1.1                    | 4.3–2.8 V w/o trickle |
| 7      | PC/LiMn <sub>2</sub> O <sub>4</sub> | 1.7                    | 8 $\mu\text{m}$ FTA | 1.1                    | 4.3–2.8 V w/o trickle |

<sup>a</sup>PC: pitch coke.

<sup>b</sup>Negative/positive capacity balance before compensation.

<sup>c</sup>Including Li on separator.

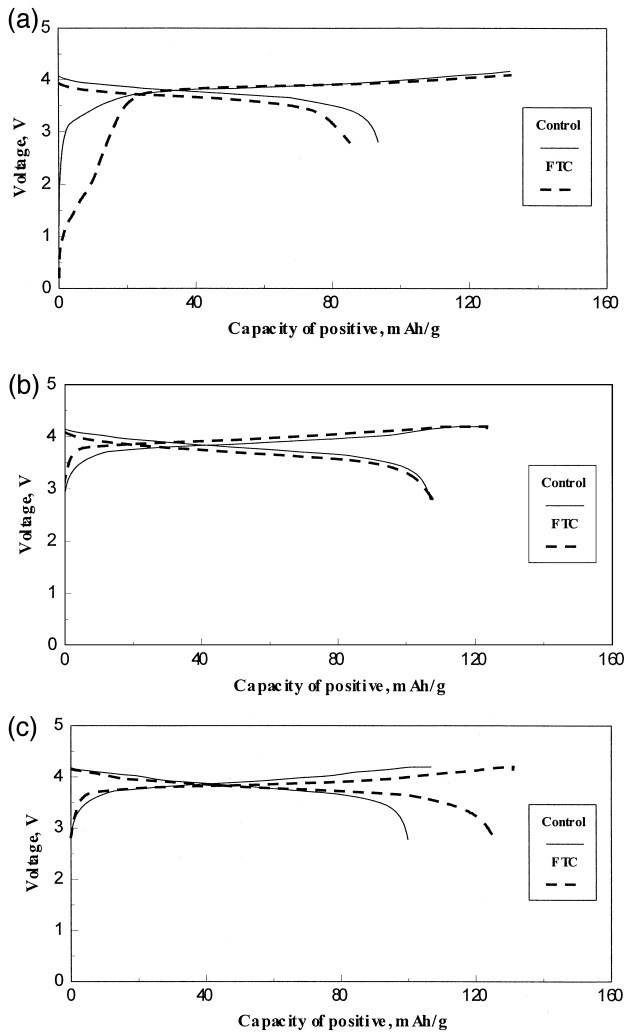


Fig. 1. Voltage profiles of Trials 1 and 2 Li-ion coin cells with and without lithium film compensation at different cycles. (a) 1st, (b) 2nd, and (c) 5th cycles.

capacity loss after 20 cycles, on the other hand, was 5% lower than control, excellent cyclability being demonstrated also.

Table 2  
Performance of Li-ion cells with or without lithium film

| Trial | Cell ID  | $Q_{P1stC}$<br>(mA h/g) | $Q_{R1stC}$<br>(mA h/g) | Efficiency<br>(%) | $Q_{R1stD}$<br>mA h/g | Irreversibility<br>(%) | $Q_{R5thD}$<br>(mA h/g,<br>mA h/cm <sup>3</sup> ) | $Q_{R20thD}$<br>(mA h/g,<br>mA h/cm <sup>3</sup> ) | Loss<br>(%) | Advantage<br>(%) |
|-------|----------|-------------------------|-------------------------|-------------------|-----------------------|------------------------|---|--|-------------|------------------|
| 1     | RS7-1    | 140                     | 132                     | 94                | 94                    | 29                     | 100/505   | 86/432   | 14          | 0                |
| 2     | RS9-3    | 166                     | 132                     | 80                | 85                    | 36                     | 130/658   | 118/598  | 9           | 30/37            |
| 3     | Bld40-22 | 120                     | 84                      | 70                | 58                    | 31                     | 64/274  | 62/265   | 3           | 0                |
| 4     | Bld40-7  | 147                     | 111                     | 76                | 77                    | 31                     | 78/394  | 68/343   | 12          | 22/10            |
| 5     | Bld40-2  | 120                     | 92                      | 77                | 75                    | 18                     | 76/384  | 73/369   | 4           | 19/18            |
| 6     | Bld40-19 | 173                     | 120                     | 70                | 83                    | 31                     | 83/419  | 79/399   | 5           | 30/27            |
| 7     | Bld40-11 | 120                     | 104                     | 84                | 93                    | 11                     | 91/460  | 86/434   | 5           | 42/39            |

$Q_{P1stC}$ : Predicted 1st charge capacity based on positive, mA h/g;  $Q_{R1stC}$ : real 1st charge capacity on positive, mA h/g; Charge efficiency;  $Q_{R1stD}$ : real 1st discharge capacity on positive, mA h/g; Irreversibility at 1st cycle;  $Q_{RnthD}$ : discharge capacity at  $n$  cycles, mA h/g or mA h/cm<sup>3</sup> based on positive; Capacity loss between 5th and 20th cycles; Capacity advantages over control at 5 and 20 cycles.

### 3.2. Pitch coke / LiMn<sub>2</sub>O<sub>4</sub> system with reduced cathode loading design

Trials 3 to 7 involved different design criteria which deducted 15% to 30% positive material based on the compensated capacity from lithium film and used 10% excess negative loading for protecting cell over charge. Two different thickness of lithium film, 4 and 8  $\mu$ m, were used in both FTC and FTA configuration. These cells employed LiMn<sub>2</sub>O<sub>4</sub> spinel material and pitch coke (heating treatment temperature, HTT, 1200°C) as positive and negative, respectively, and were cycled by a constant current of 1 mA (0.4 mA/cm<sup>2</sup>) between 4.3 and 2.8 V up to 30 cycles.

Fig. 2(a) and (b) illustrates the voltage profiles of control cells and cells with lithium film (FTC configuration) at first cycle in terms of positive and negative capacities, respectively. A low voltage plateau was observed in cells with lithium film during the charge, repeating the result observed in Trial 2 in which different positive (lithium cobalt oxide) material was used. It should be noted that the capacity of the plateau is proportional to the thickness of lithium film. The more lithium in cell, the larger the plateau capacity. Clearly, the lithium film from the composite material is involved in active cycling to provide higher charge and discharge capacities. The irreversibility of these cells, on the other hand, were almost unchanged, although the cells with the lithium film deliver much higher positive specific capacity due to less positive materials loading. Capacity calculation based on negative materials that were kept constant also indicated the capacity increase contributed by lithium.

Fig. 3(a) and (b) shows the voltage profiles of cells with lithium film FTA configuration in the comparison with control cells at first cycle. The charge voltages of cells with lithium composite were 0.5 to 1.0 V higher than that of control, suggesting strongly that the negative electrode had been partially lithiated soon after the cells were assembled and prior to cycling. The lower negative specific capacity in FTA cells, as indicated in Fig. 3(b), is an

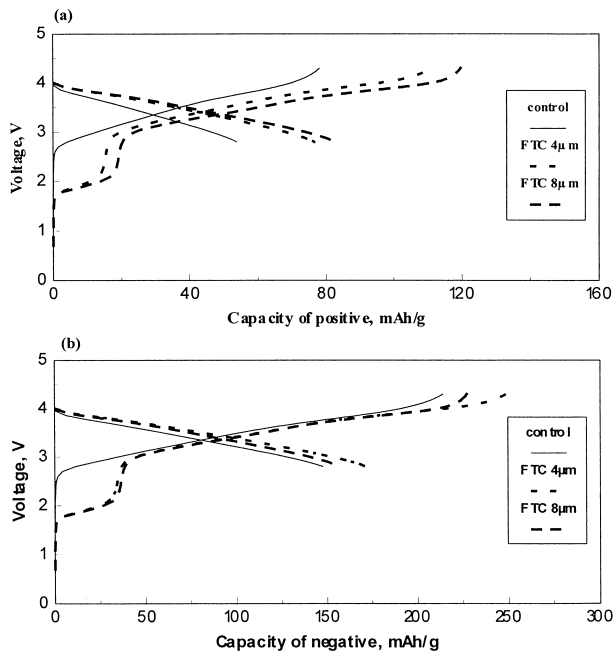


Fig. 2. Voltage profiles of Trials 3 to 5 Li-ion coin cells with and without lithium film compensation at first cycles. FTC 4  $\mu\text{m}$ : 4  $\mu\text{m}$  lithium FTC configuration; FTC 8  $\mu\text{m}$ : 8  $\mu\text{m}$  lithium FTC configuration.

indication of a so-called pre-lithiation process as well. Clearly again, the lithium composite on the separator was very efficiently involved in cell chemical reaction. As a result, low irreversibility can be seen in cells with lithium film (18% and 11% for 4 and 8  $\mu\text{m}$  lithium film, respectively), compared to 31% of control cell.

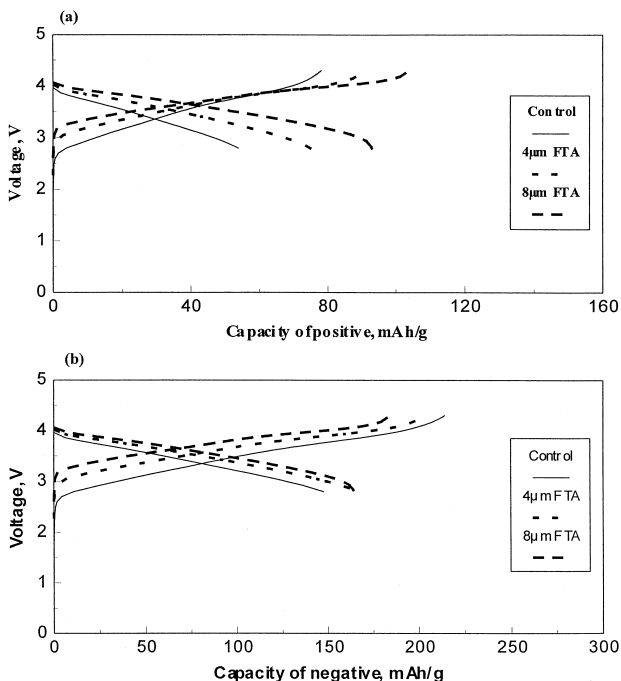


Fig. 3. Voltage profiles of Trials 3 to 5 Li-ion coin cells with and without lithium film compensation at first cycles. FTA 4  $\mu\text{m}$ : 4  $\mu\text{m}$  lithium FTA configuration; FTA 8  $\mu\text{m}$ : 8  $\mu\text{m}$  lithium FTA configuration.

In order to understand the details of lithiation processes, in which lithium composite material provides a key rule to change the chemistry of Li-ion cell, statistical analysis was conducted based on the data at cycle one. Fig. 4(a) to (d) shows these results in terms of charge and discharge capacities, charge efficiency, and irreversibility. In terms of charge capacity, thick film (8  $\mu\text{m}$ ) provides significantly higher capacity than thin (4  $\mu\text{m}$ ) film and control. The highest capacity of 140 mA h/g (from the mean plot in Fig. 4(a) based on the positive) was reached in 8  $\mu\text{m}$  FTC cells. The charge efficiency, which is defined by the ratio of real charge capacity to the predicated capacity from lithium compensation, on the other hand, varied with lithium film configuration and the thickness of lithium film. No difference was found between FTC and control cells. This suggests that in the FTC configuration, compensation may occur via a more complicated mechanism, which requires a few more cycles to completely incorpo-

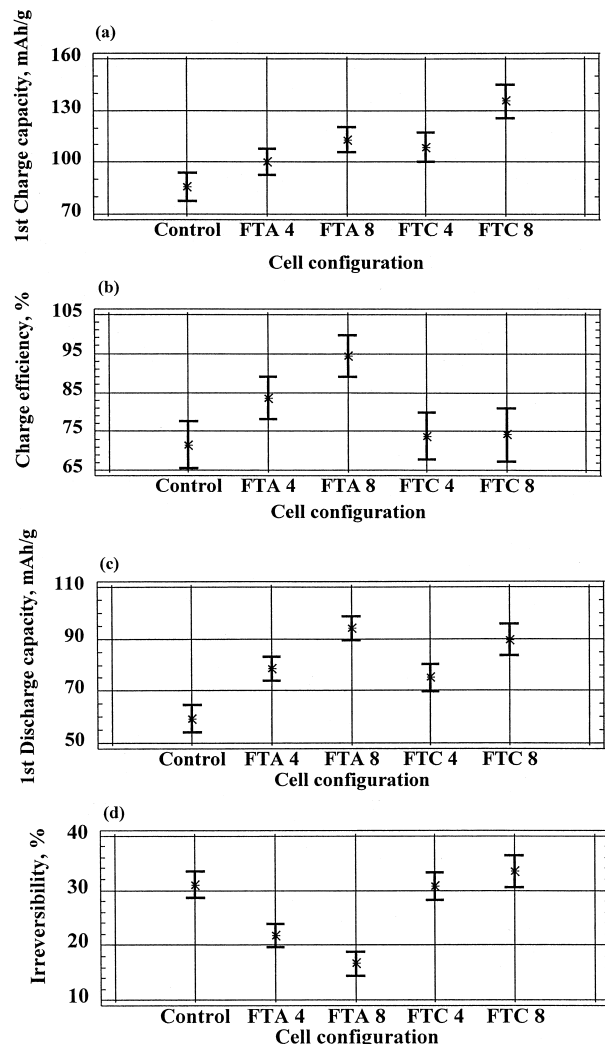


Fig. 4. Mean plot of cell performance data for different group cells. (a) Positive capacity at 1st charge; (b) charge efficiency; (c) positive capacity at 1st discharge; and (d) irreversibility at 1st cycle.

rate all capacity from the lithium film, as has been indicated in Trial 2 in Fig. 1. Two FTA groups, on the other hand, have very higher charge efficiency (greater than 80%, Fig. 4(b)) which indicates the high efficiency of in situ pre-lithiation process as shown in the voltage profiles of Fig. 3. The charge efficiency increases with the thickness of lithium film, suggesting that the volumetrically efficient lithium film would reduce the overall irreversibility of cell. Because of the increased efficiency due to the lithium film, all cells compensated by lithium film displayed higher discharge capacity at the end of the 1st cycle. The more lithium in the cell, the higher the specific capacity due to reduced positive loading as seen in Fig. 4(c). As a result, significant improvement in irreversibility was obtained in FTA configuration, typically the 8  $\mu\text{m}$  film configuration. As low as 16% irreversibility was demonstrated in 8  $\mu\text{m}$  FTA as indicated in Fig. 4(d). FTC configuration, on the other hand, does not compensate capacity directly to the negative. No direct improvement in irreversibility, therefore, is expected, although much higher cell and electrode capacity has been demonstrated due to the high efficiency of the lithium film discussed above.

Table 2 summarizes the overall performance of a typical cell in each group in terms of charge efficiency and irreversibility at the 1st cycle, discharge capacities of cells at cycles 5 and 20, capacity loss during the cycling, and the performance improvement of cells compensated with Li over the control cells. These data clearly indicate that cells with lithium film in both FTC and FTA configuration

can deliver higher specific and volumetric capacities, around 30% improvement being obtained. Fig. 5(a–b) illustrates the cyclability of these cells over 30 cycles in terms of specific and volumetric capacities based on positive material. Higher volumetric capacity of this design is the most attracting benefit. Excellent cyclability has been demonstrated as well.

#### 4. Discussion

Data presented in this study have clearly indicated that a thin lithium film deposited on the separator can become efficiently involved in the cell reaction during active cycling, delivering high capacity to compensate capacity loss due to irreversible reaction on the negative electrode and within cell. Cell design using reduced positive material loading can deliver much higher volumetric capacity, and therefore, energy density due to the high efficiency of lithium. Significant reduction in irreversibility also contributes to high-energy density design. Li-ion cell with high density energy, therefore, eventually can be designed based on this concept.

Although it has been demonstrated that the thin lithium film is rapidly involved in cell reactions in each configuration, several processes including ionization of lithium film into the electrolyte, diffusion across the porous separator, and lithiation of each electrode might be involved during the first few cycles.

In the case of FTA configuration, the reaction is much faster. It has been thought that the lithiation of carbon negative electrode is spontaneous once physical contact between lithium metal and carbon occurs soon after filling with electrolyte. The open circled voltages (OCV) of cells upon filling with electrolyte were around 1.5 to 2.0 V, compared to less than 50 mV of normal Li-ion cells. Such a significant increase in OCV and the high running voltage at 1st charge are considered as the indication of the lithiation processes. Good agreement between film thickness and voltage increase in Fig. 3(a) and (b) suggest that such processes might be efficient when sufficient, but not an over-balanced lithium is provided. Improvement in reducing irreversibility during the first cycle is the direct benefit from the lithiation completed by compensation. The processes usually can be accomplished at the first cycle, providing quick and significant chemical reaction in the cell.

On the other hand, in the FTC configuration, the lithium film on the separator might form a bipolar cell in which lithium performs as a third electrode to deliver capacity to each electrode once the cell is charged [6]. The voltage plateau seen during the first charge is a clear indication that lithium is reacting first and across the porous separator to start lithiating the negative, or to lithiate the positive material typical in the case of using spinel material. In

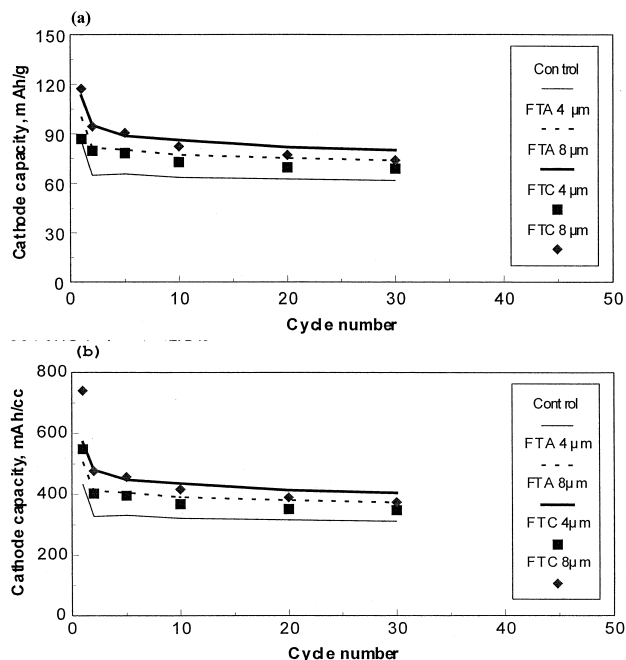


Fig. 5. Cyclability of Li-ion coin cells with or without lithium film compensation. Both FTA and FTC cells deliver high reversible specific and volumetric capacities and excellent cyclability up to 30 cycles. (a) Specific capacity of positive vs. cycle numbers, (b) volumetric capacity of positive vs. cycle numbers.

each case, the thin lithium film provides compensated capacity to maintain high efficient cycling processes between the two electrodes. High lithium content was found in lithium cobalt oxide positive electrode compensated by lithium film and cycled up to 30 cycles (Trial 2). This suggests that lithium not only improves cell capacity through direct activation and reaction, but also maintains a high lithium content in the positive material to keep good cyclability. Since this is a much slower process than that occurs in FTA configuration, a few cycles of formation are normally necessary. High rate charge may also accelerate the processes to enhance the delivering of lithium to the electrodes. On the other hand, the relatively high irreversibility at the first cycle, as indicated in Table 2, may be due to the decomposition of positive materials caused by the direct contact between metallic lithium and positive electrode before the cell was charged.

Because of the excellent cyclability of cell compensated by lithium film, this concept may be a solution to improve the poor cyclability of spinel materials at high temperature and to improve the performance of hard carbon materials. Also, this technology may provide a revolution for polymer-based Li-ion battery in which highly efficient thin electrode fabrication is essential and critical.

Although the compensation seems to be efficient in terms of performance improvement, the utilization of lithium film in the present study is still considered low. In ideal conditions, cell with FTA configuration should have close to zero irreversibility and the FTC cell should have close to 100% charge efficiency. More efficient cell design such as wound cell design and using relatively high rate formation regions may help improve the efficiency.

Another concern that we must address here is the safety of the cell. Although no safety test data has been reported

in this study, the postmortem of cycled cells indicated no lithium film was found on either separator or electrodes. Also, there is a question about how violent the spontaneous lithiation in electrolyte may be because the reaction may result in electrolyte decomposition and gas release. Our experiments, however, did not experience such conditions. As the lithium film is so thin and the reaction only takes place in the first few cycles, we conclude that cell behavior will be very much similar to the traditional Li-ion cell in terms of most cell characteristics.

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