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Cycling performance of low-cost lithium ion batteries with natural graphite and $LiFePO_4$

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Abstract

Low-cost lithium ion batteries with $LiFePO_4$ and natural graphite were cycled in 1M $LiBF_4$+EC/DEC at 100% depth of discharge and 25^{o}C in order to investigate cycle performance and diagnostics for capacity fading. The 12cm^2-pouch cell showed 65% of capacity retention at 5C compared to that of capacity at C/25. The cell showed 80% of initial capacity after 80 cycles and its capacity fade rate was 11.3μAh/cycle during constant C/2 cycling. In hybrid pulse power characterization, the discharge resistance of this cell was higher than commercial graphite/$LiCoO_2$ cell because of low lithium diffusivity in $LiFePO_4$. Slow rate cycling in pouch full cell showed almost 40% of capacity fading after 100 cycles. However, 100-cycled cathode and anode did not show any capacity fading in half-cell test after disassembling full cell, suggesting that capacity fade in the full cell is caused by loss of cycleable Li.

Keywords; Lithium-ion batteries, natural graphite, $LiFePO_4$

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Introduction

The interest in lithium rechargeable batteries in electric vehicles (EVs) has been significantly increased in recent years [1-3]. The important factors for their application are low price, long cycle life, environmental safety, and high specific energy.

The carbonaceous materials, graphite, as lithium intercalation compound and the replacement of lithium metal anode have shown high capacity and good cycling performance. However, synthetic graphite commonly employed in the anode of commercial lithium rechargeable batteries, is expensive compared to natural graphite

Transition metal oxides such as $LiCoO_2$, $LiNiO_2$ and spinel $LiMn_2O_4$ have been studied as cathode materials in lithium batteries. These materials have shown good cyclibility and high capacity at high potential (around 4V vs. Li/Li^+). Spinel compounds, such as $LiMn_2O_4$, are promising candidates because of low toxicity and cost compared to $LiCoO_2$ and $LiNiO_2$, but they still have problems with Mn dissolution and they are low energy density. Recently, the phosphate $LiFePO_4$ has been studied as the cathode-active material in Li batteries, because of it's expected low-cost, low toxicity and high theoretical specific capacity of 170mAh/g [4,5].

In this work, we assembled and tested low-cost lithium ion cells with $LiFePO_4$ and natural graphite in liquid electrolyte. The cycle performance, life, and impedance characteristics of this cell are reported, along with some post-test, electrochemical diagnostics of the components after cycling.

Experimental

Electrodes for the pouch cell were supplied by Hydro-Québec (IREQ). The anode consisted of natural graphite (87%) and PVdF binder (13%) on Cu foil current collector. The cathode consisted of carbon-coated $LiFePO_4$ (82%) from Univ. de Montreal, carbon (8%) and PVdF binder (10%) on carbon-coated Al foil current collector. These electrodes were dried under vacuum at 120°C for 12 h before cell assembly inside an Ar atmosphere glovebox. Electrodes were cut and assembled into metal Swagelok cells ($1cm^2$) or Al-laminated pouch cells ($12cm^2$) with Celgard separator and 1M $LiBF_4$+EC/DEC (1/1).

After pouch cell assembly, the cell was formed with 2 cycles at very slow rate (C/25) to form smooth SEI layer on the surface of electrode [6,7]. The voltage range of 2.5 – 4.0V was used for 100% DOD cycling. After cycling, the pouch cell was disassembled for electrochemical and other analysis in the glovebox. Each component was washed in dimethyl carbonate solution for 24 hours and dried at 60^oC in vacuum before testing. Cell testing and post-test analysis of electrode components were carried out with Maccor battery cycler and the lower current Arbin battery cycler, respectively.

Results and Discussion

Cycle performance of pouch cell

Fig. 1 shows voltage profiles for discharge of the $LiFePO_4$ and natural graphite pouch cell at various C rates. The cut-off voltages were 2.5V and 2.0V for C/5-C/1 and 2C-5C, respectively. The charge for all cycles was C/2. Average voltage for discharge decreased from 3.3V (C/5) to 2.6V (5C) with increase C rate. From our results in half-cell, the $LiFePO_4$ cathode was strongly affected by C rate, probably because of low electric conductivity and/or lithium diffusivity in $LiFePO_4$. Despite this, the cell shows reasonable capacity retention at high rate. Fig. 2 shows the discharge capacity retention of different cells at various C rates. C_{max} is the discharge capacity at slow rate (C/25). The doped $LiNiO_2$/graphite cell was prepared in a similar method with Fuji $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and Hitachi MAG-10 graphite [8]. Although the capacity retention of $LiFePO_4$/natural graphite cell is slightly lower than doped $LiNiO_2$/synthetic graphite cell, this cell shows good capacity retention and the capacity retention at 2C and 5C is 81 and 65%, respectively.

Fig. 3 shows the cycle performance and coulombic efficiency of the pouch cell during constant (C/2) cycling over 100% DOD. The discharge capacity decreased linearly to 80% of initial capacity at 80th cycle. The initial C/2 capacity corresponds to 82mAh/g-$LiFePO_4$

(0.4mAh/cm^2). Low utilization continues to be a problem with $LiFePO_4$, even at low rates. However, when this is combined with the irreversible capacity loss of the anode, the problem is more extreme. The capacity fade rate during C/2 cycling was 11.3 μAh/cycle and capacity at 200th cycle can be expected to 50% of initial capacity. As shown in Fig. 3, the average coulombic efficiency for this cell was about 99.4%. The reasons for the capacity fade will be discussed below.

The impedance characteristics of the cell were measured with a modified version of the Hybrid pulse power characterization (HPPC) test developed by PNGV (Partnership for a New Generation of Vehicles) [2,9]. After charging, the cell was discharged at C/2 to 90% SOC and a 18s (3C) discharging pulse, followed by a 10s (2.25C) charge pulse were applied. This was continued at intervals of 10% SOC. Fig. 4 shows the voltage profiles for the fresh and 100-cycled cell during HPPC test. Although the fresh cell showed pulse power capability at full range of depth of discharge (DOD), after 100 cycles the cell lost pulse power at 60% of DOD. Fig. 5 shows the discharge resistance, as area-specific impedance (ASI), and pulse power capability for fresh and cycled cells. After 100 cycles, the discharge resistance of the cell increased significantly, especially at high DOD.

Diagnostics for capacity fading

After the C/2 cycling, we cycled the cell again for comparison with formation. Slow rate cycling is used for understanding the reasons for capacity fade, such as structural fracture, conductivity loss or active material loss. Fig. 6 shows voltage profiles for the slow rate cycling at first and second cycles and after 100 cycles. The first and second cycles show irreversible capacity losses (ICL) of 27% and 6%, respectively. From half-cell test of each electrode, the $LiFePO_4$ cathode material showed less than 5% ICL for the first cycle and the coulombic efficiency of $LiFePO_4$ of second cycle was almost 100%. However, the half-cell test of the graphite electrode showed 28% and 11% of ICL for the first and second cycle, respectively. Therefore, we attribute most of ICL in the pouch cells to the graphite anode. When we assemble the pouch cell, the expected capacity ratio between cathode and anode was 1:1.1 to prevent the formation of lithium metal on the anode surface. Although the cathode was fully charged on the first cycle, the utilization of cathode after the first two cycles decreased to 82% because of high irreversible capacity loss of anode.

We stopped constant C/2 cycling at 100th cycle where capacity fade was 23% from initial capacity of C/2. Fig. 6 shows the slow rate cycle of C/25 after 100 cycles. The discharge capacity at C/25 (0.32mAh/cm^2) dropped 40% after 100 cycles compared to that of fresh cell (0.54mAh/cm^2). This capacity loss for slow rate cycling is higher that for constant C/2 cycle, which was 23%.

Fig. 7 shows dQ/dV plots for slow rate cycles of fresh and 100-cycle cells. In the fresh cell, there are three peaks for charge and discharge. Each peak is assigned to the lithium intercalation/deintercalation into/from graphite layer [10,11] because $LiFePO_4$ has only one plateau for charge and discharge [4]. However, after 100 cycles, the third high voltage peak disappeared in dQ/dV plot. The third peak for lithium intercalation in graphite is assigned to region I at the lowest potential, which is related to the reaction of lithium with graphite between LiC_{12} and LiC_6 [11]. This means that the anode in the pouch cell was not fully charged to final stage because of capacity fading.

In order to further elucidate the mechanism for capacity fade, we carried out electrochemical half-cell tests for each electrode after disassembling the fully-discharged pouch cell, and washing. Fig. 8 shows the voltage profiles of fresh and cycled electrodes against fresh lithium metal foil at slow rate of C/25 in half-cell. On the first charge of the $LiFePO_4$ cathode sample (Fig. 8a), only about 50% of the expected Li was recovered. However, the next cycle showed a capacity for Li similar to that in the fresh electrode. This means that $LiFePO_4$ cathode in the pouch cell was discharged to only 50% during final slow rate cycle of C/25. The anode was fully discharged as removed from the cell, and showed a voltage profile very similar to the fresh anode (Fig. 8b). Neither electrode showed any capacity fading in half-cell test. Only 50% of lithium in $LiFePO_4$ was utilized in pouch cell at final cycle and the other 50% of lithium was not active in cycling. We can be confident that the main reason of capacity fading in full cell does not come from electrodes. 18% of lithium from $LiFePO_4$ in the pouch cell was used for the formation of SEI layer on the anode and 21% of lithium was consumed during cycling. Further diagnostics are required to completely understand the nature of the side reactions in this system. Incompatibility between the $LiBF_4$ electrolyte and the natural graphite is a possibility.

Conclusions

$LiFePO_4$/natural graphite lithium ion cell was cycled in $LiBF_4$ containing electrolyte at 100% DOD and room temperature. The cell showed rapid capacity fading during constant C/2 cycling and its discharge capacity at 80th cycle was 80% of initial capacity. This cell for first and second slow rate cycles showed 18% of irreversible capacity loss (ICL). After 100 cycles, the discharge capacity of final cycle at slow rate showed 40% of capacity fading. However, after disassembling the pouch cell, the results for each electrode from half-cell test showed that the cathode and the anode did not show any capacity fading in spite of rapid capacity loss of the pouch cell. The capacity fade was attributed to the loss of cycleable Li by side reactions during cycling, not to structural or physical problem of electrodes.

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List of figures

Fig. 1. Voltage profiles of $LiFePO_4$/graphite cells at various C rates. Charge rate C/2.

Fig. 2 Capacity retention of $LiFePO_4$/graphite cell at various C rates. (◆) $LiFePO_4$/natural graphite cell; (☐) $LiNi_{0.8}Co_{0.15}Al_{0.05}$/graphite cell.

Fig. 3. Cycle performance and coulomb efficiency of $LiFePO_4$/graphite cell at C/2 rate. (◇) Capacity retention; (☐) Coulombic efficiency.

Fig. 4. Hybrid pulse power characterization test as function of depth of discharge (DOD). (a) Fresh cell; (b) 100-cycled cell; Charging pulse 2.25C, discharging pulse 3C.

Fig. 5. Discharge resistances and pulse power capabilities of fresh and cycled cell. (◆,◇) Fresh cell; (☐,■) after 100 cycles

Fig. 6. Voltage profiles at first, second cycles and after 100 cycles at C/25

Fig. 7. dQ/dV plots for slow rate cycles of fresh and 100-cycled cells. (a) Fresh cell; (b) 100-cycled cell.

Fig. 8. Voltage profiles of fresh and cycled electrodes in half-cell. (a) $LiFePO_4$; (b) graphite.

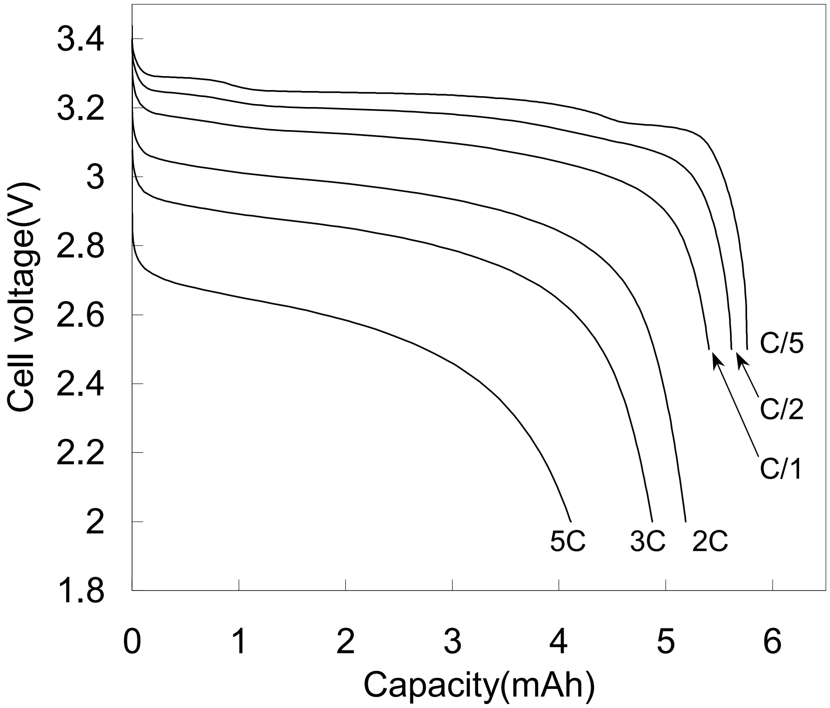
Cell voltage(V)
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
0
1
2
3
4
5
6
Capacity(mAh)
C/5
C/2
C/1
5C
3C
2C

Fig. 1

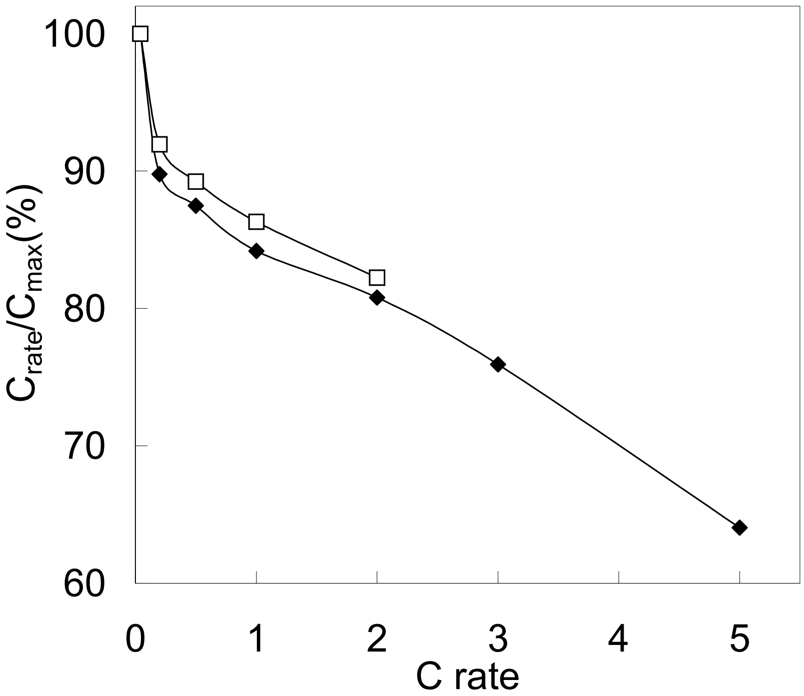

Fig. 2

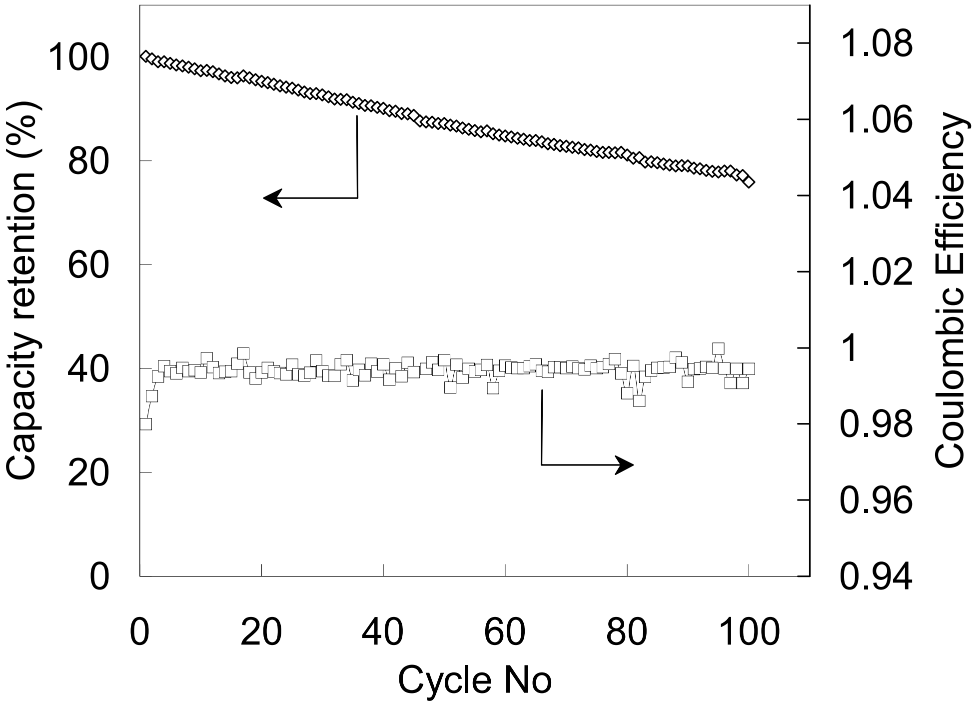
Capacity retention (%)
0
20
40
60
80
100
Coulombic Efficiency
0.94
0.96
0.98
1
1.02
1.04
1.06
1.08
Cycle No
0
20
40
60
80
100

Fig. 3

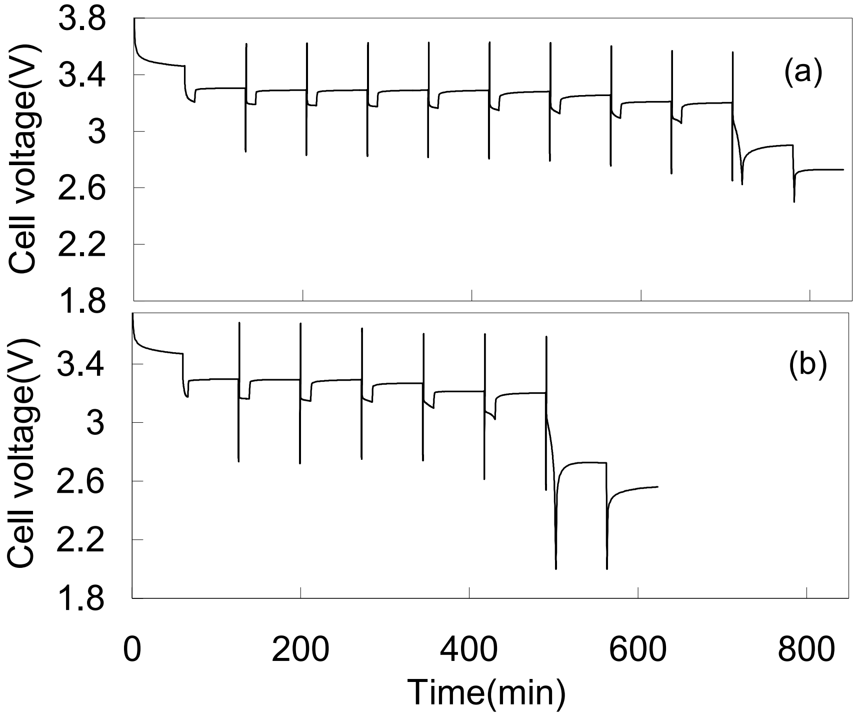
3.8
3.4
3
2.6
2.2
1.8
Cell voltage(V)
(a)
3.4
3
2.6
2.2
1.8
Cell voltage(V)
(b)
0
200
400
600
800
Time(min)

Fig. 4

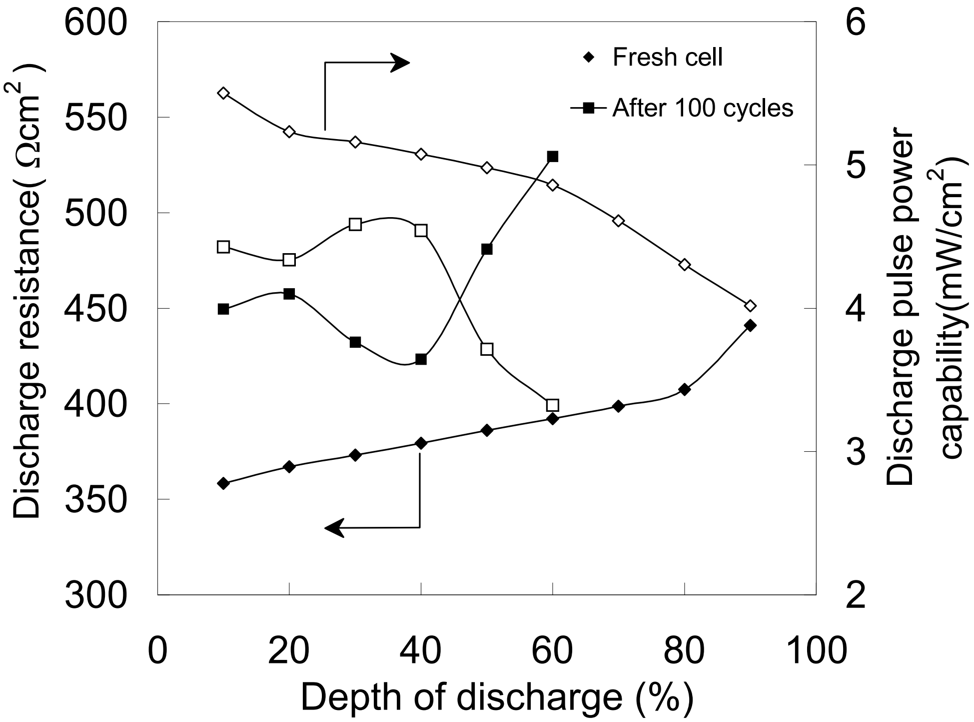
Discharge resistance(Ωcm2)
600
550
500
450
400
350
300
0
20
40
60
80
100
Depth of discharge (%)
6
5
4
3
2
Discharge pulse power capability(mW/cm2)
◆ Fresh cell
■ After 100 cycles

Fig. 5

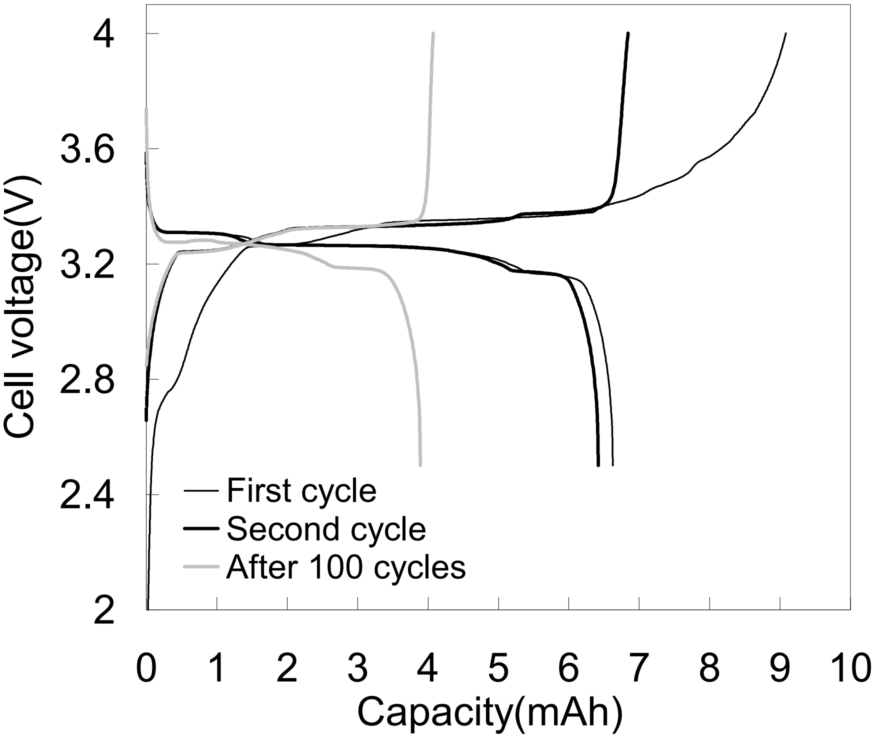
Cell voltage(V)
4
3.6
3.2
2.8
2.4
2
Capacity(mAh)
0
1
2
3
4
5
6
7
8
9
10
First cycle
Second cycle
After 100 cycles

Fig. 6

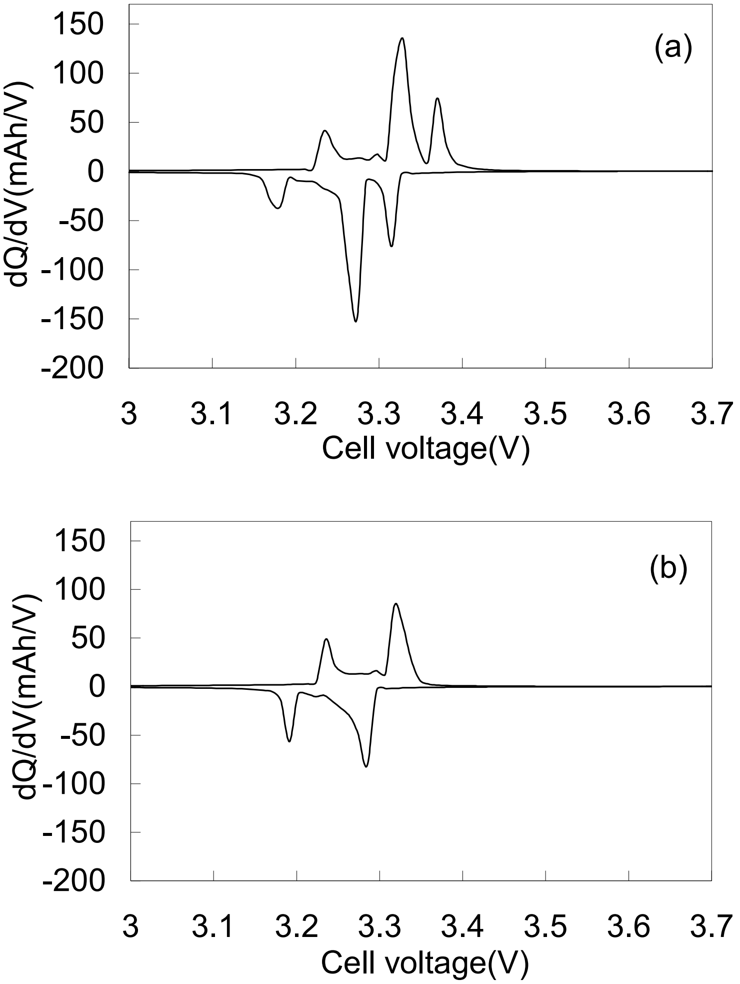
(a)
dQ/dV(mAh/V)
150
100
50
0
-50
-100
-150
-200
3
3.1
3.2
3.3
3.4
3.5
3.6
3.7
Cell voltage(V)
(b)
dQ/dV(mAh/V)
150
100
50
0
-50
-100
-150
-200
3
3.1
3.2
3.3
3.4
3.5
3.6
3.7
Cell voltage(V)

Fig. 7

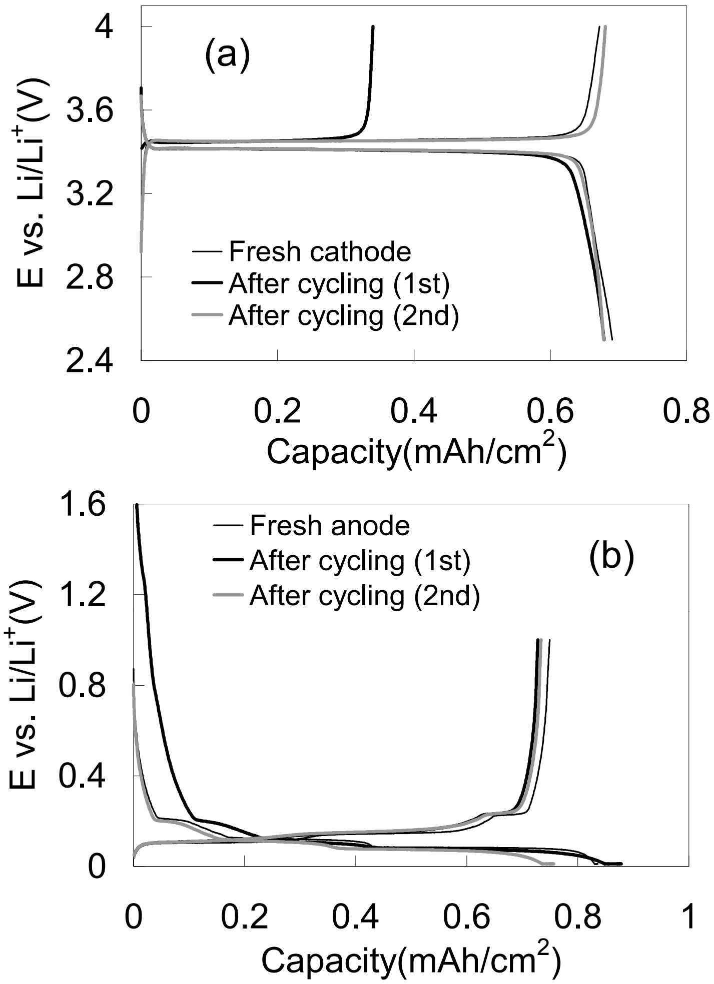
(a)
E vs. Li/Li$^+$(V)
4
3.6
3.2
2.8
2.4
0
0.2
0.4
0.6
0.8
Capacity(mAh/cm^2)
Fresh cathode
After cycling (1st)
After cycling (2nd)
(b)
E vs. Li/Li$^+$(V)
1.6
1.2
0.8
0.4
0
0
0.2
0.4
0.6
0.8
1
Capacity(mAh/cm^2)
Fresh anode
After cycling (1st)
After cycling (2nd)

Fig. 8