

Cycling performance of low-cost lithium ion batteries with natural graphite and LiFePO₄

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Abstract

Low-cost lithium ion batteries with LiFePO₄ and natural graphite were cycled in 1 M LiBF₄ + EC/DEC at 100% depth of discharge and 25 °C in order to investigate cycle performance and diagnostics for capacity fading. The 12 cm² pouch cell showed 65% of capacity retention at 5C compared to that at C/25. The cell showed 80% of initial capacity after 80 cycles and its capacity fade rate was 11.3 μA h/cycle during constant C/2 cycling. In hybrid pulse power characterization, the discharge resistance of this cell was higher than commercial graphite/LiCoO₂ cell because of low lithium diffusivity in LiFePO₄. Slow rate cycling in pouch full cell showed almost 40% of capacity fade after 100 cycles. However, the 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.

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1. 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 LiCoO₂, LiNiO₂ and spinel LiMn₂O₄ have been studied as cathode materials in lithium batteries. These materials have shown good cyclibility and high capacity at high potential (around 4 V versus Li/Li⁺). Spinel compounds, such as LiMn₂O₄, are promising candidates because of low toxicity and cost compared to LiCoO₂ and LiNiO₂, but they still have problems with Mn dissolution and they are low energy density. Recently, the phosphate LiFePO₄ has been studied as the cathode-active material in Li batteries, because of it is expected low-cost,

low toxicity and high theoretical specific capacity of 170 mA h/g [4,5].

In this work, we assembled and tested low-cost lithium ion cells with LiFePO₄ 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.

2. 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 LiFePO₄ (82%) from University 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 (1 cm²) or Al-laminated pouch cells (12 cm²) with Celgard separator and 1 M LiBF₄ + 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 2.5–4.0 V was used for 100% depth of discharge (DOD)

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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 h and dried at 60 °C in vacuum before testing. Cell testing and post-test analysis of electrode components were carried out with a Maccor battery cycler and the lower current Arbin battery cycler, respectively.

3. Results and discussion

3.1. Cycle performance of pouch cell

Fig. 1 shows voltage profiles for discharge of the LiFePO₄ and natural graphite pouch cell at various C rates. The cut-off voltages were 2.5 and 2.0 V for C/5–C/1 and 2C–5C, respectively. The charge for all cycles was C/2. Average voltage for discharge decreased from 3.3 V (C/5) to 2.6 V (5C) with increased C rate. From our results in half-cells, the LiFePO₄ cathode was strongly affected by C rate, probably because of low electric conductivity and/or lithium diffusivity in LiFePO₄. 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 LiNiO₂/graphite cell was prepared in a similar method with Fuji LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ and Hitachi MAG-10 graphite [8]. Although the capacity retention of LiFePO₄/natural graphite cell is slightly lower than doped LiNiO₂/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 the 80th cycle. The initial C/2 capacity corresponds to 82 mA h/g LiFePO₄ (0.4 mA h/cm²). Low utilization continues to be a problem with LiFePO₄, even at low rates. However, when this is combined

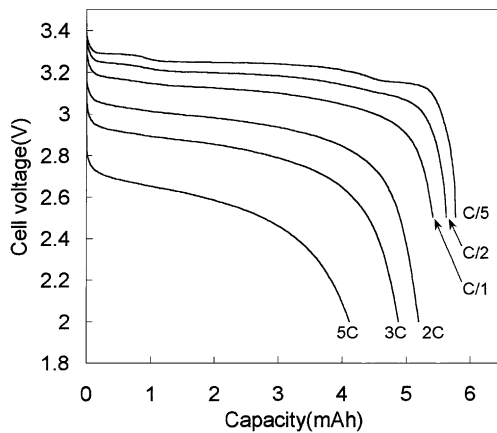


Fig. 1. Voltage profiles of LiFePO₄/graphite cells at various C rates. Charge rate C/2.

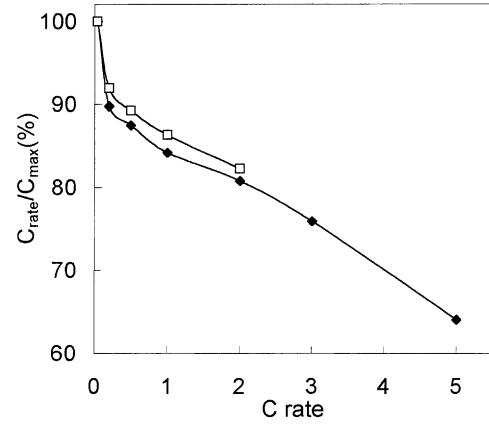


Fig. 2. Capacity retention of LiFePO₄/graphite cell at various C rates. (◆) LiFePO₄/natural graphite cell; (□) LiNi_{0.8}Co_{0.15}Al_{0.05}/graphite cell.

with the irreversible capacity loss (ICL) of the anode, the problem is more extreme. The capacity fade rate during C/2 cycling was 11.3 μA h/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 later.

The impedance characteristics of the cell were measured with a modified version of the hybrid pulse power characterization (HPPC) test developed by partnership for a new generation of vehicles (PNGV) [2,9]. After charging, the cell was discharged at C/2 to 90% SOC and a 18 s (3C) discharging pulse, followed by a 10 s (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 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.

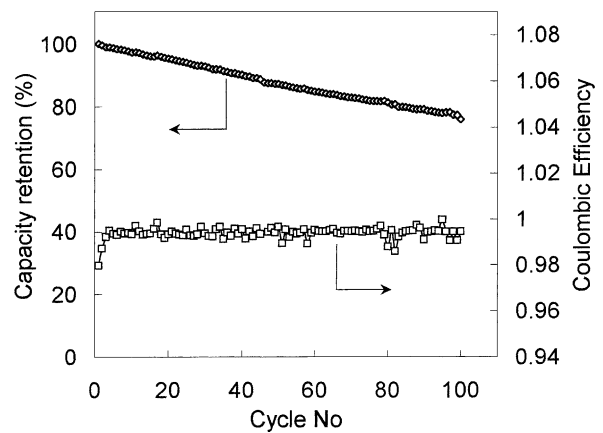


Fig. 3. Cycle performance and coulomb efficiency of LiFePO₄/graphite cell at C/2 rate. (◇) Capacity retention; (□) coulombic efficiency.

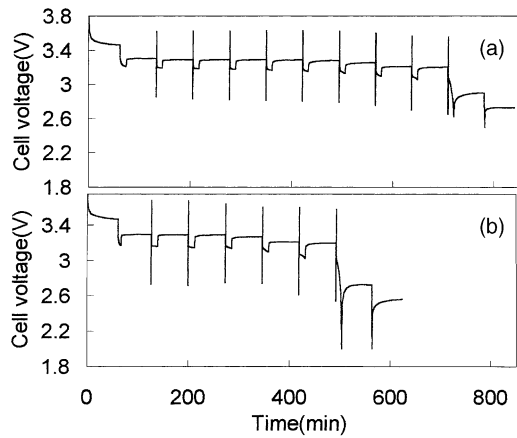


Fig. 4. Hybrid pulse power characterization test as function of depth of discharge (DOD). (a) Fresh cell; (b) 100-cycled cell; charging pulse 2.25C, discharging pulse 3C.

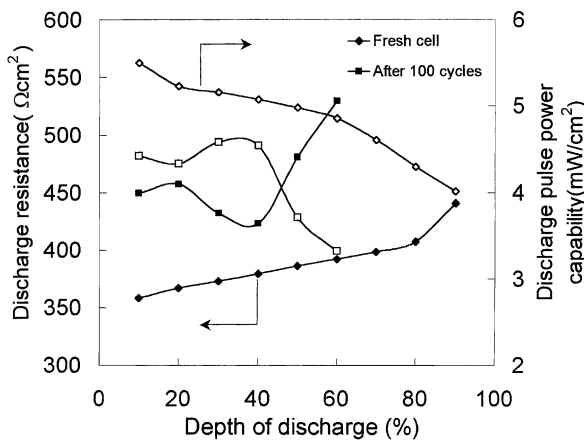


Fig. 5. Discharge resistances and pulse power capabilities of fresh and cycled cell. (◆, ◇) Fresh cell; (□, ■) after 100 cycles.

3.2. 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 ICL of 27 and 6%, respectively. From half-cell tests of each electrode, the LiFePO_4 cathode material showed <5% ICL for the first cycle and the coulombic efficiency of LiFePO_4 for the second cycle was almost 100%. However, the half-cell test of the graphite electrode showed 28 and 11% ICL for the first and second cycle, respectively. Therefore, we attribute most of the 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.

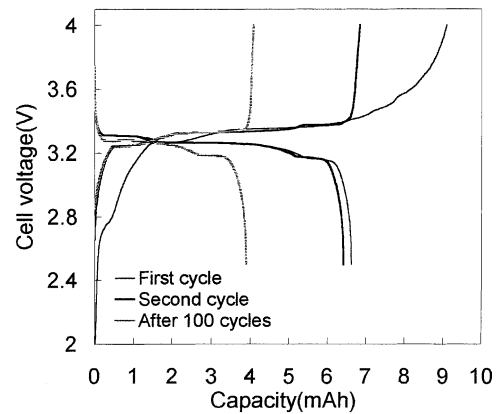


Fig. 6. Voltage profiles at first, second cycles and after 100 cycles at $C/25$.

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

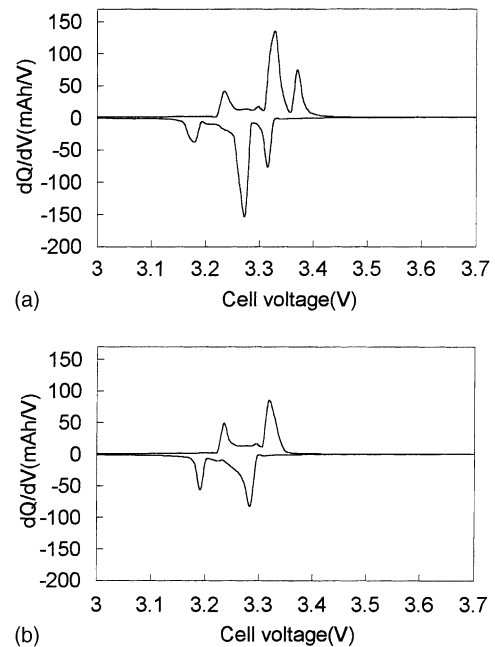


Fig. 7. dQ/dV plots for slow rate cycles of fresh and 100-cycled cells. (a) Fresh cell; (b) 100-cycled cell.

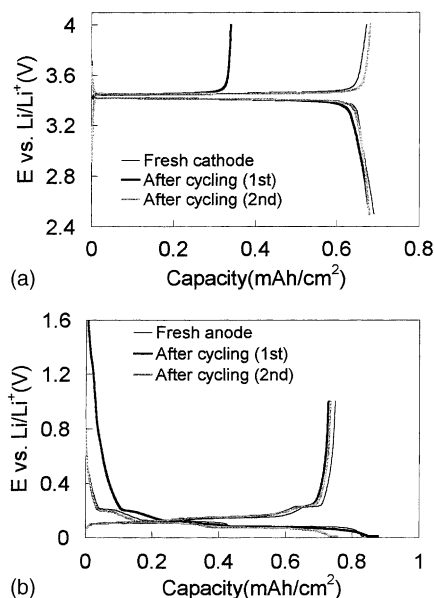


Fig. 8. Voltage profiles of fresh and cycled electrodes in half-cell. (a) LiFePO_4 ; (b) graphite.

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 the 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 at $C/25$. 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 the half-cell test. Only 50% of the lithium in LiFePO_4 was utilized in the pouch cell during the final cycle and the other 50% of lithium was not active in cycling. We can be confident that the capacity fading in the full cell is not due to degradation of the structure of either electrode. Instead, this behavior is consistent with the consumption of the cycleable lithium through a side reaction. Eighteen percent of the lithium from the LiFePO_4 in the pouch cell was consumed during the reduction of the electrolyte during the formation of SEI layer on the anode. Twenty-one percent of lithium was consumed during cycling. The side-reaction could be due to an instability of the SEI layer on the anode leading to continual reformation of this layer or trace water in the cell. Further diagnostics are required to completely understand the nature of the side

reactions in this cell. Incompatibility between the LiBF_4 electrolyte and the natural graphite is a possibility.

4. Conclusions

A LiFePO_4 /natural graphite lithium ion cell was cycled in LiBF_4 -containing electrolyte at 100% DOD and room temperature. The first and second slow rate (formation) cycles showed 18% ICL. The cell showed rapid capacity fading during constant-current cycling at $C/2$ and the discharge capacity at the 80th cycle was 80% of initial capacity. After 100 cycles, the discharge capacity of the final cycle at slow rate showed a 40% loss in capacity compared with the formation cycle. However, after disassembling the pouch cell, half-cell studies of the cathode and 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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