LiFePO$_4$/gel/natural graphite cells for the BATT program

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Abstract

LiFePO$_4$/gel/natural graphite (NG) cells have been prepared and cycled under a fixed protocol for cycle and calendar life determination. Cell compression of 68 kPa was found to represent an optimal balance between cell impedance and the first cycle losses on the individual electrodes with the gel electrolyte. Cells with a Li anode showed capacities of 160 and 78 mAh/g LiFePO$_4$ for C/25 and 2C discharge rates, respectively. Rapid capacity and power fade were observed in the LiFePO$_4$/gel/NG cells during cycling and calendar life studies. Diagnostic evaluations point to the consumption of cycleable Li though a side reaction as the reason for performance fade with minimal degradation of the individual electrodes.
Published by Elsevier Science B.V.

Keywords: LiFePO$_4$/gel/natural graphite cells; BATT program; Calendar life test

1. Introduction

Recently, Li-ion gel polymer batteries have been commercialized for portable electronic devices, using costly LiCoO$_2$ in the cathode. Polymer Li-ion batteries have thickness and weight advantages over liquid electrolyte cells due to the use of the laminated "film bag" packaging materials [1]. However, lower-cost materials are required for the application of Li-ion batteries in EV and HEV applications [2].

In the Batteries for Advanced Transportation Technologies (BATT) program, we are developing thin Li-ion gel batteries whose low cost, performance and safety should be superior to classical Li-ion batteries, using carbon-coated LiFePO$_4$ from the Université de Montreal (UdM) in the cathode. The cells contain a high viscosity electrolyte, based on LiBF$_4$ salts and a mixture of carbonate solvents. Herein we report the cell performance and the characteristics of materials for thin Li-ion batteries using LiFePO$_4$ in the cathode and high purity natural graphite in the anode. In addition, the interfaces between the electrodes and the separator layer have been studied with impedance spectroscopy.

2. Experimental

The thin Li-ion gel batteries were constructed at Hydro-Québec (HQ–IREQ) using UdM's LiFePO$_4$ active material in the cathode, HQ natural graphite in the anode and a gel electrolyte based on a polyether added to liquid electrolyte: LiBF$_4$ (EC + EMC). Cells were constructed both from pure cross-linked gels and gels coated onto a Celgard® membranes before crosslinking. Cells were constructed in several configurations including anode versus cathode and anode or cathode versus a Li foil counter electrode. The effect of cell-pack compression on interface phenomena were analyzed by ac impedance spectroscopy at 68, 136 and 204 kPa. For performance testing, cells were sealed into aluminum–plastic laminated film pouches and studied at the optimum compression of 68 kPa. The charge–discharge characteristics were evaluated at several rates between the voltage limits of 2.5–4 V. Continuous cell cycling out 120 cycles at a rate of C/2 with periodic measurements of cell impedance was carried out with the Maccor Battery Cycler.

3. Results

The effect of cell compression on the electrode performance was studied in the cell configurations: Li/gel
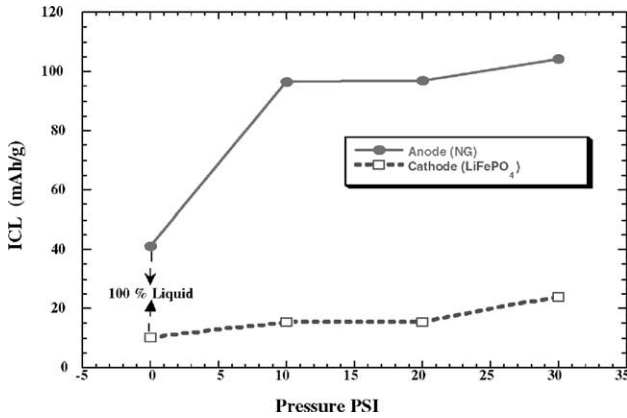

Fig. 1. Dependence of first cycle irreversible capacity loss (ICL) on cell compression with gel electrolyte and Li anode.

polymer/graphite, and Li/gel polymer/LiFePO$_4$ without Celgard$^®$ membranes. The effect of pressure on the first cycle irreversible capacity loss (ICL) is shown in Fig. 1. Not shown is the drop-off in reversible capacity for the anode and cathode at 136 and 204 kPa, respectively. From these studies, and impedance measurements, an optimum compression of 68 kPa was determined and used for the remainder of the cell testing.

3.1. Cell cycling

All cells were subject to two formation cycles at a rate of C/25 (about 6.3 mA/g) to form a stable SEI layer on the carbon anode and to characterize the loading of the cell. These are shown as differential capacity (dQ/dV) plots for cells with the different configurations in Fig. 2. The LiFePO$_4$ electrode shows a single set of peaks for the phase-transition.
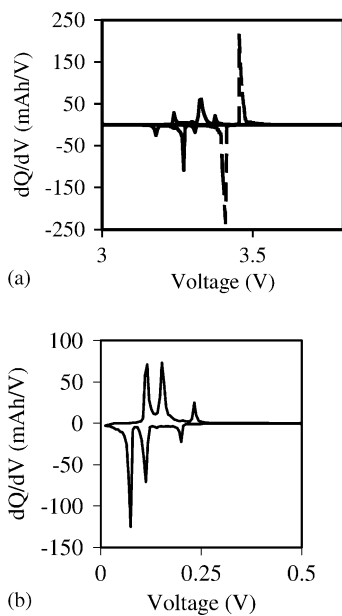

Fig. 2. Formation of the three types of cell: (A) LiFePO$_4$/NG (—) and LiFePO$_4$/Li (- - -); (B) NG/Li.
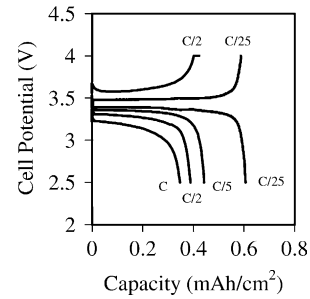

Fig. 3. Variable rate discharge profiles for a LiFePO$_4$/Li cell with gel electrolyte.

The HQ natural graphite shows three peaks, consistent with previous results. The LiFePO$_4$/gel/NG cell shows the three graphite peaks shifted to higher potential.

The three configurations of cells were evaluated with gel electrolyte at a range of discharge capacities. The LiFePO$_4$/ Li with a gel-coated Celgard$^®$ separator and a lithium metal anode showed high reversible capacity at 25 °C (162 mAh/ g) and low discharge rates. The capacities delivered at a C/25 and a series of higher discharge rates (with a C/2 charge) are shown in Fig. 3. The cyclability of the LiFePO$_4$/NG cells with pure gel and gel-coated Celgard$^®$ electrolyte are shown in Fig. 4. The first 20 cycles correspond to the variable rate discharge cycles. The average discharge capacity as a function of rate for the full cells are compared in Fig. 5 along with a comparable cell with liquid electrolyte (no gel) and a
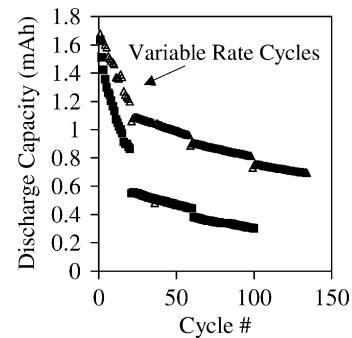

Fig. 4. Cycling summary for two LiFePO$_4$/NG cells (△) gel/Celgard$^®$ and (■) gel only.
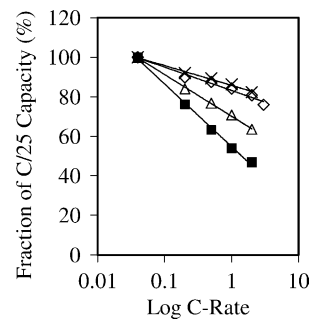

Fig. 5. Fraction of low-rate discharge capacity recovered in LiFePO$_4$/NG cells at high-rate, with three electrolyte systems: (△) gel/Celgard$^®$, (■) gel only, (◇) liquid electrolyte and (×) an HEV (ATD) high-power cell.

pouch cell constructed with a high-power cell chemistry including a $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$-containing cathode [3]. Cycles 21–120 were carried out at a constant rate of *C*/2, with periodic interruption of the cycling for pulse power testing. It is clear that the capacities of the $LiFePO_4$/NG cells are fading at unacceptably high rates both with and without the Celgard® membrane.

3.2. Calendar life testing

In order to examine the reasons for this high fade rate, a similar cell (with Celgard®) was studied in a calendar life test. After formation, the impedance was measured (discussed below) and then it was charged to 3.3 V (close to 100% SOC). The cell was left at OC except for the application of a discharge pulse and several charge-compensating charge pulses per day [4]. In addition, the *C*/2 capacity was measured about once per week and the cell was returned to 3.3 V. The rates of capacity fade for the cycled and calendar life tests are shown in Fig. 6 to be quite similar when examined from the time of the initial formation. The data are shown versus the time from formation, or the first addition of Li to the anode. From full-spectrum impedance measurements before testing it was found that the cell impedance was stable during cold storage (10 °C) for a few weeks. Other evidence with the Li-anode cells suggests a possibly different fade mechanism, since the impedance of these cells was also relatively stable on storage. It is clear that the stability of the gel electrolyte components is an issue.

3.3. Impedance/pulse power testing

Periodic pulse measurements for these cells were carried out as a function of SOC with a slightly modified version of the PNGV HPPC profile [4]. The area specific impedance (ASI), calculated from the 18 s discharge pulse, increased steadily with cycle number and time, as summarized in Fig. 7. The pulse measurements were analyzed further to understand which components of the impedance are changing [5]. The initial (ohmic) voltage drop (500 ms) was subtracted from the total voltage drop after 18 s in order to estimate a "polarization ASI" from these data. The ohmic
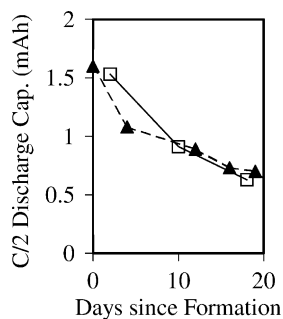

Fig. 6. Capacity fade of two similar cells during calendar (□) and cycle life (▲) testing.
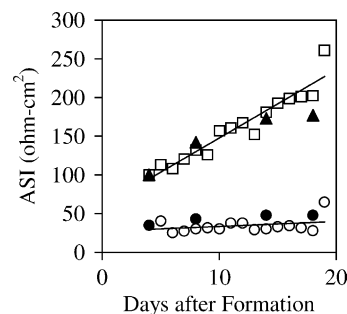

Fig. 7. Changes in the total cell impedance with calendar (□) and cycle life (▲) testing. The polarization component (○ and ●) is more stable.

portion of the total ASI will contain contributions from the electronic and ionic resistivity in the solid and liquid phases, respectively. It will also include any film resistances building up on the interfaces. The polarization ASI will include overpotentials due to lithium concentration gradients in the solid active materials or electrolyte phases and the resulting thermodynamic potentials associated with them. The polarization ASI is also shown in Fig. 7. It is clear that the polarization resistance is fairly constant for these cells, suggesting that the diffusion paths for the lithium in the cell are unchanged. However, the initial ohmic drop on application of the pulse increases with time regardless of whether or not the cell is cycled. This is probably due to an increased interfacial resistance due to surface film growth during testing. It is not possible to distinguish between resistances on the anodes or cathode with this measurement.

3.4. Electrochemical diagnostics

One cell was examined further after cycling. The cell was disassembled inside the glovebox and portions of the electrodes were assembled without washing, into a Swagelok cell with a Li–metal counter electrode, a Celgard® separator and LP40 electrolyte (1M $LiPF_6$/EC/DEC). The electrode pieces were discharged and then cycled at *C*/25. The voltage profiles for this post-test diagnostic are shown in Fig. 8. The cathode was at about 47% SOC and the anode was at 2.8 V versus Li, or essentially 0% SOC as disassembled from the discharged gel cell. These profiles are compared with the same test carried out with freshly formed electrodes of the same composition and loading tested against Li in 1.0 M $LiBF_4$/EC/DMC electrolyte [3]. The cycled cathode recovers essentially the same capacity as that of the fresh electrode suggesting that the structure of the $LiFePO_4$ remains intact. This was confirmed with XRD (not shown). The anode appears to have lost some of the capacity present in the fresh electrode. In addition, the definition of the plateaus in this curve are obscured in this test, consistent with higher resistance in this electrode. This could easily be attributed to components of side-reaction products remaining on the electrode surface and slowing the interfacial kinetics. Further diagnostic analysis of the cell components will be the subject of a later contribution.
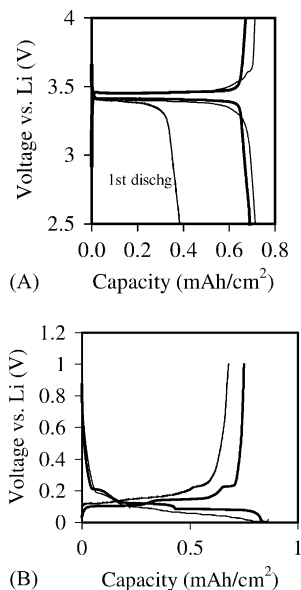
Fig. 8. *C*/25 cycling of LiFePO$_4$/gel/NG cell components after cycling (—) compared with fresh electrode data (—). (A) Cathode vs. Li; (B) anode vs. Li.

The capacity loss in the cell can be attributed directly to a chemical consumption of the cycleable Li from the cell with the natural graphite anode. However, the LiFePO$_4$/Li cell showed even higher rates of capacity fade. It is clear that the gel electrolyte is unstable in this system. The chemical reaction does not start until the anode reaches a reducing potential (graphite cells were stable until formation). The reaction products form a layer on the electrodes leading to the observed rise in cell ASI. Further diagnostics are underway to determine the nature of this reaction.

3.5. Conclusions

Pouch cells were assembled with low-cost components and gel electrolytes in various configurations for performance testing. An optimum cell-pack compression of 68 kPa was determined. The maintenance of the capacity at high discharge rates was strongly influenced by the electrolyte, as opposed to the LiFePO$_4$ electrode. Stability of the capacity and impedance for cells with the gel electrolyte is a big concern whether or not the cells are cycled. Post-test electrochemical diagnostics suggest that side reactions that consume the cycleable lithium in the cell and increase interfacial resistance of the anode are directly responsible for the fade in performance. Improvements in the chemical compatibility between the gel and the electrode components should lead to a very promising low-cost rechargeable Li battery.

Acknowledgements

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