The Transformation of Graphite Electrode Materials in Lithium-ion Batteries

After Cycling

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Abstract

To reveal how graphite electrodes change with cycling in lithium-ion batteries, electrochemical experiments involving charge-discharge cycling at different current density conditions are performed on commercial pouch cells and the graphite electrodes after cycling. This research shows that the polyvinylidene fluoride (PVDF) binder does not degrade, confirmed by the stable molecular weight after different cycling conditions. Particle size analysis results indicate that the diameter of graphite particles after cycling is ~10% larger than that of the graphite before cycling, which results in a ~30% volume expansion after cycling. For the cells cycled at the same current density, the graphite particle size increases with cycle time. For the cells with the same cycle numbers, the graphite particle size is larger in the cells cycled at lower current density. X-ray diffraction characterization shows that the *d*-spacings of the graphite particles in all the cells at different cycling conditions are identical. These results suggest that the graphite particle size increase associated with cycling may arise specifically when primary particles inflate the secondary particle size, leading to dramatic volume expansion of graphite secondary particles.

1. Introduction

With increasing demands for energy, it becomes more and more important to diversify energy sources and to develop sources other than fossil fuels. To use “clean” and sustainable energy sources, such as solar and wind, even more effective energy storage systems (ESS) need to be developed to ensure around-the-clock energy delivery and to mediate power fluctuations [1]. As the most widely used ESS, batteries—especially lithium-ion batteries—have drawn significant research attention due to their unique advantage of high energy density (up to 150 Wh kg^{-1}) [2-4].

To meet increasing demand for low-cost, long-life and high-energy-density EES, cathode materials and anode materials for lithium-ion batteries have been widely studied. Many commercialized systems already exist for cathode material such as LiCoO_2 [5], LiMn_2O_4 [6], $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ [7], $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ [8] and LiFePO_4 [9]. Although several novel materials show promising performance [10-15], carbon material is still the usual commercial host for storing lithium ions in the negative electrodes of lithium-ion batteries. Variation during cycling, such as particle size change, morphology change, and the interface chemistry, is important for long-term cycling performance [16]. Aurbach and colleagues have shown that graphite electrodes failed due to the cracked graphite particles and thick solid electrolyte interface (SEI) on graphite surface [17-19]. Therefore, studies of graphite electrodes in lithium-ion batteries help in understanding the failure mechanism of the batteries.

Lithium iron phosphate (LiFePO_4) combined with graphite lithium-ion battery chemistry is one of the most promising candidates, not only because of the abundance

of iron element and carbon materials, but also due to their stable cycle performance [20-22], where stationary storage for electric grid application demands tens of thousands of cycles per installation. In the most recent progress, commercial graphite/LiFePO₄ cells have demonstrated thousands of stable cycles [23-25]. Since LiFePO₄ works at a lower potential, the failure of positive electrode is minimal [26]. Long-term failure is exclusively due to the consumption of electrolyte by the carbon anode. The electrolyte “starvation” leads to the final cell failure. Replenishing the electrolyte leads to almost total recovery of the cell capacity. [27-29]

With this in mind, this study investigated the stability of binder and graphite particles in the negative electrodes in a group of commercial LFP/graphite lithium-ion rechargeable cells. First cells were cycled with galvanostatic charge-discharge in different C-rates and cycle time and then disassembled to obtain the cycled PVDF polymer binder and graphite in negative electrodes. The stability of binder during the electrochemical tests was examined by studying the variation of molecular weight of polymer binder in different cycling conditions using gel permeation chromatography (GPC) method. The graphite particles were investigated by using a particle size analyzer (PSA), X-ray diffraction (XRD), and a scanning electron microscope (SEM). The stability of the PVDF binder and the transformation of the carbon active materials are the main focus of this investigation.

2. Experimental section

2.1 Battery information

The commercial polymer pouch cells studied consist of LFP as the cathode and graphite as the anode with a PVDF binder. The designed capacity of each cell is 1 Ah. The cells were custom fabricated by ATL Co. (Fig. 1a) The PVDF binder material and graphite anode material were analyzed and documented before they were used. The formation of these cells was done before shipping to Lawrence Berkeley National Laboratory for testing and analyses.

2.2 Battery tests

The galvanostatic charge-discharge tests were performed on those cells using Maccor 4000 at 30°C between 3V and 4V and at different C-rates. Some cells were cycled 200 times at 0.2C, 0.5C, 1C, or 4C, and some cells were cycled 400, 600, or 800 times at 1C-rate. One cell was fully charged and periodically recharged to maintain the fully charged state at the time other cells were being cycled. All the cells were charged and discharged two times at 0.1C and stopped at their discharged state for material harvesting and analyses.

2.3 Preparation of anode samples for GPC, PSA, SEM, and XRD tests

All the cells were disassembled in a glove box filled with argon. The anodes were washed in dimethyl carbonate (DMC) thoroughly and dried in the glove box at room temperature. The dried graphite anode samples were then used for the following experiments (Fig. 1b, c).

2.4 GPC measurements

Pieces with areas of 10 cm × 10 cm were cut from the anodes and were soaked in 5 mL N-Methylpyrrolidone (NMP) for three days to dissolve the binders in the electrode laminate. Then the mixtures were filtered to remove the particles to obtain clear PVDF/NMP solutions for GPC analyses. The molecular weight of PVDF polymer binder was determined by use of a Waters 1515 Series HPLC equipped with a refractive index detector. A Styragel 4.6 × 300 mm column (Waters) was employed with NMP eluent (0.3 mL min⁻¹) and calibrated by using polystyrene standard samples (Agilent Technologies) in NMP.

2.5 PSA, SEM, and XRD tests

About 3cm × 7cm of the dried graphite laminate was cut from each electrode. Twenty mL of NMP was added and the mixture was sonicated for 3.5 hours. After copper current collector was removed, the mixture was centrifuged. After the top layer of NMP solvent was decanted, the graphite precipitate was washed with 20 mL deionized water and centrifuged again. After the NMP and water wash process was repeated twice, the graphite was collected and dried at 60 °C for 12 hours. The dry powders were ready for PSA, SEM, and XRD experiments. Fifty mg of graphite powder was mixed with Darvan C surfactant and the mixture was sonicated for 15 minutes. The graphite suspension was then injected in the laser diffraction particle size analyzer (Beckman Coulter LS230). The morphology of powders were imaged with a JEOL JSM-7500F field emission SEM. XRD experiments were performed on a Philips X'Pert Pro Multipurpose X-ray Diffractometer using Cu K α radiation (λ = 0.15406 nm).

3. Results and discussion

3.1 Charge and discharge properties at different rates

Figure 2a shows the charge-discharge curves of the third cycle at different C-rates for LFP/graphite lithium-ion cells at 30 °C. The curves of the third cycle are stable enough to represent the characteristic curves for LFP/graphite lithium-ion cells at different test conditions. Before testing, all the LFP/graphite pouch cells have experienced formation procedure in the ATL factory before being shipped to Berkeley National Laboratory for analyses. The discharge curve at 0.2 C rate shows three plateaus, which is consistent with the fact that LFP positive material has a very flat plateau at 3.5 V, and the graphite has three plateaus during the working voltage. The average discharge voltage for 0.2C, 0.5C, 1C, and 4C is 3.25, 3.2, 3.2, and 3.1 V, respectively. The relatively high working voltage indicates the relatively small internal resistance of all the LFP/graphite cells, which are produced with the same material and processed with excellent uniformity. The pouch cells can be charged up to 1036, 1026, 1013, and 660 mAh capacity at 0.2C, 0.5C, 1.0C, and 4C. It is noted that the charged capacity ratio for 4C vs. 0.2C is 63.7%, which means the cell can be charged up to 63.7% of its full capacity in 15 minutes (fast charge mode).

3.2 Stability of PVDF binder

To study the stability of PVDF in different cycling conditions, the cells were cycled 200 times at 0.2C, 0.5C, 1C, 2C, and 4C and 400, 600, and 800 times at 1C, along with a cell cycled twice at 0.1C. Then all the cells were disassembled and the stability

of the PVDF binder were investigated. All the cells were charge-discharged two times after the cycling test to ensure that they were fully discharged before they were opened. Fig.3 shows the cycling stability and columbic efficiency at different charge-discharge procedures. Most cells show excellent cycling performance at 0.2C, 0.5C and 1C, and the columbic efficiency is near 100%. The reversible capacities at those C-rates are close to 100% of their design capacity of 1000 mAh. After 800 cycles at 1C, the capacity retention is 91.6%. However, the cell, which is set to cycle 400 times at 1C rate, shows fast fading after 180 stable cycles, then the capacity rises slightly after the 200th cycle. The columbic efficiency of this cell is normal, then becomes very unstable after 180 cycles. The capacity of this cell fully recovered in the last 0.1C charge and discharge. The accessible cycling capacity at 4C is around 60% of its designed capacity while the cell capacity also fully recovered to the designed capacity of 1000 mAh at 0.1 C cycling. The full recovery suggests that the fast fading for 1C 400 cycles and 4C is due to the high cut-off voltage of 3.0 V. The impedance increase during cycling causes the voltage plateau decrease. At 4C, the cut-off voltage is on the plateau, so a small move down from the plateau can lead to a large capacity drop.

The overall excellent rate of performance and cycling stability are due to the stable performance of LiFePO₄ and the outstanding electrode and cell design and fabrication. Therefore, it is a perfect system to understand how the anode is transformed after extended cycling. The main focus of this study is on the gradual transformation of the PVDF binder and graphite materials in the anode electrode. All the data acquired from

the abnormal cells is marked; however, the discussion of abnormality of the cells is out of the scope of this study.

GPC is based on size exclusion chromatography (SEC) theory, which separates analytes on the basis of size. The technique is often used for the analysis of polymers. GPC separates based on the size or hydrodynamic volume (radius of gyration) of the analytes. This differs from other separation techniques that depend on chemical or physical interactions to separate analytes. The decomposition of polymers normally associates the breaking of chemical bonds of the polymer chains. If the PVDF is decomposed into short molecular weight polymers during cycling, the radius of gyration of the polymer will shrink, therefore its peak position or peak width in the GPC analysis will change. Figure 4 shows the results of GPC tests for all the PVDF samples after different charge-discharge tests. Both peak position or peak width are the same in allowable error. Therefore, the PVDF is stable in all the tested cells regardless of C rate or cycle number. Even for the 1C 400 cycles cell, the capacity and columbic efficiency becomes noisy in the last 200 cycle, but the PVDF still shows no decomposition. It suggests that the PVDF is chemically stable during cycling. There is no decomposition of the PVDF binders in the anode during the extended period of testing.

3.3 Transformation of graphite anode material

Figure 5 shows the typical particle size distribution and Figure 6 shows typical XRD spectrum of the graphite samples. The results are summarized in Table 1 and plotted in Figure 7. First, there is no difference between the particle size of pristine

graphite and pristine graphite after sonication for 3.5 hrs, indicating that graphite particle size does not change during the cleaning process with sonication. The graphite particle size increases rapidly during the first few days of cycling. After the initial fast expansion, the graphite particle size increases continuously with cycled time. A pseudo linear relationship between the particle size and cycled time can be observed. As discussed in the previous study by Aurbach, et al. [17-19], thickness of SEI layer increases significantly with prolonged cycling in their lithium-graphite electrode. However, it is not possible that the increase of the graphite particle size in this study is also due to the growth of SEI on the surface of secondary particles during cycling. The morphology evolution of the secondary graphite particles of the fresh powder to the cycled powder does not support the formation of a high degree of SEI on the secondary particles. Since there is a poor linear relation between d-spacing and cycle time, we believe that the particle size increase does not come from the crystallographic change of the graphite primary particles. The cell stayed at top of the charge, whose anode was fully lithiated and kept at this stage for more than 100 days. The cell does not show any significant change of particle size or d-spacing. This further confirms that the graphite particle size change is not due to the d-spacing enlargement when lithium-ion storage between the graphene layers is prolonged. The study also shows that the average graphite particle diameter increases more than 10% for the cells that were cycled more than 200 times. A ten percent increase in diameter results in ~ 30% volume expansion. For the cell that was cycled at 1C 800 times, the particle diameter increase is ~20% and the volume expansion is larger than 70%. This

particle size enlargement of graphite is mainly due to the cycling effect. It is interesting to notice that the graphite particle size increase is proportional to the cycle time in the linear region, not cycle numbers. Different C-rates cycling, when plotted by cycle times, forms a linear relationship with the particle diameter expansion. The particles, which have the largest volume expansion, are not from the cell with the most cycles, but from the cell that had the most cycle hours. Such a significant size and volume change of graphite particles has never been reported to the knowledge of this research team.

Figure 8 shows three SEM images of the pristine graphite powder and graphite particle from the cycled cells. It is confirmed that the graphite particles from cycled cells were cleaned very well. No obvious aggregation of the graphite particle is found. Combined with the particle size change from above, it can be concluded that the graphite particles did not break down into smaller particles during cycling since graphite particle size does not decrease.

To reveal the possible reason for the secondary graphite particle size change, we proposed the reorganization of the primary particles within the secondary particles as the root cause of the volume expansion. The reorganization of primary graphite particles is due to the lattice parameter change during lithiation and delithiation. The reorganization of primary particles lead to crack formation in the secondary particles, and a possible influx of electrolyte within the secondary particle cracks, leading to SEI layer growth on the primary particles. Although this additional SEI on the surface of primary particles is not observable in the SEM in Figure 8, it is partially supported

by the observation of electrolyte depletion of the graphite/LFP cells by the battery industry. Generally speaking, SEI layer growth increases cell impedance during cycling. However, comparing the voltage profiles of the first and 800th cycle of the cell cycled at 1C after 800 times (Figure 2b), the study shows that the overpotential grows only slightly over time, which indicates that the cell impedance does not increase significantly. This implies that the large particle size increase in this cell, which is around 30%, is not explained by the SEI layer growth. The porosity increase of the secondary particles must also play a key role to the graphite particle size increase. The effect of volume expansion to the performance is two folds. First, the volume expansion creates new surface, therefore consuming electrolyte, leading to electrolyte starvation after extended cycling. Second, the severe volume expansion leads to continue cell swelling, leading to lower volumetric energy density in the later stage of the cell life. Both discussions are now included in the text.

Conclusions

This study investigated the stability of PVDF and graphite particles in graphite anodes. LiFePO₄ batteries were galvanostatic charge-discharged at different C rates and for different times. The GPC tests show the PVDF is stable in all the tested batteries and the capacity fading is irrelevant to PVDF degradation. Particle size analysis results indicate that the graphite particle size of cells after they were cycled was ~10% larger than the average diameter of the cell before cycling, which results in a ~30% volume expansion after cycling. For the cells cycled at the same current density, the graphite particle size increased with cycle time. For the cells with the

same cycle numbers, the graphite particle size was larger in the cells cycled with smaller current density. XRD characterization showed that the d-spacing of the graphite particles in all the cells was very similar. All of these results suggest that graphite particle size increase with cycling arises from either SEI formation in the primary particles or a porosity increase in the secondary particles.

Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency, Vehicle Technologies Office of the U.S. Department of Energy under the Advanced Battery Materials Research (BMR) Program and Applied Battery Research (ABR) Program. Electron microscopy experiments were conducted at the National Center for Electron Microscopy (NCEM). The NCEM is located at Lawrence Berkeley National Laboratory (LBL), and is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under contract No. DE-AC02-05CH11231. This work was also supported by the Fundamental Research Funds for the Central Universities of China (N110802002), the National Natural Science Foundation of China (51204038).

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Table 1. Summary of electrochemical performance, particle size and d-spacing of the studied graphite samples

Sample ID	Cycle procedure	Initial Capacity (mAh)	Decay per cycle (%)	D ₅₀ (μm)	d-spacing (Å)
ATL pristine	N/A			10.65	3.387
ATL029	0.1C 2 cycles	1042		11.08	3.383
ATL008	0.5C 200 cycles	1027	0.029	12.09	3.417
ATL043	1C 200 cycles	1012	0.026	11.61	3.415
ATL055	1C 400 cycles	1013	0.035	11.74	
ATL070	1C 600 cycles	1007	0.016	11.76	
ATL054	1C 800 cycles	1009	0.011	12.56	3.410
ATL046	4C 200 cycles	660	0.13	11.50	3.365
ATL069	4C 1000 cycles	778	0.097	11.42	
ATL050	Top charge			10.40	3.377

Figure captions

Fig. 1. Pouch cell fabricated by ATL. a. The pouch cell and dimension (The scale is in centimeter). b. The jelly-roll after open the pouch cell. c. The electrode laminates after open the jelly-roll.

Fig. 2. (a) The voltage profiles of the third cycle at different C-rates for LFP/graphite lithium-ion cells at 30 °C, and the charge rate is the same to the discharge rate. (b) The voltage profiles of the first and 800th cycle of the cell cycled at 1C for 800 times. 1C=1 A.

Fig. 3. (a) Discharge capacity and (b) columbic efficiency versus cycle numbers for LFP/graphite lithium-ion cells tested at different charge-discharge procedures at 30 °C. 1C=1 A.

Fig. 4. GPC measurements of PVdF binders after cycling in the electrode. a. 0.1C 2 cycles, b. 0.5C 200 cycles, c. 1C 200 cycles, d. 1C 400 cycles, e. 1C 800 cycles, f. 4C 200 cycles, g. 0.2C 200 cycles.

Fig. 5. Size distribution of the graphite particles from negative electrodes of ATL pouch cells.

Fig. 6. Typical XRD patterns of graphite samples.

Fig. 7. Correlation between the particle size/d-spacing with cycle time for the cells.

Fig. 8. SEM images of a. pristine, b. 1C 800 cycles, c. 4C 200 cycles, d. 0.5C 200 cycles

Figure1

Figure2a

Figure2b

Figure3a

Figure3b

Figure4

Figure5

Figure6

Figure7

Figure8