Changes of Anode Materials during Extended Cycling of Lithium Ion Batteries

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Abstract

Experimental data on lithium ion batteries with LiCoO 2 as cathode and SSG (a modified natural graphite) as anode showing good uniformity, high capacity and good cycling behavior are reported. Three cells were cycled for 500, 1060 and 1600 cycles, the changes of the graphitic anode material were investigated by X-ray diffraction, scanning electronic microscopy, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, cyclic voltammetry and capacity measurements in order to identify the mechanism of capacity fading of these lithium ion batteries. During cycling, the graphitic structure is very stable and evidently does not change. However, the electrolyte solution continuously reacts with the anode material during cycling and the thickness of the surface film on the anode material increases with cycling, which leads to a change of the surface composition, increase of charge transfer resistance and decrease of the height of redox peaks in cyclic voltammograms. The comparison of the capacity fading of the anode material and the complete lithium ion batteries shows clearly that the anode mainly contributes to capacity fading of lithium ion batteries due to reactions of electrolyte solution constituents with the anode material during cycling. These results provide valuable clues for manufacturing lithium ion batteries with improved cycling behavior.

Keywords: Lithium ion battery; Capacity fading; Anode; Graphitic carbon; Surface film.

Introduction

The cycling behavior of lithium ion batteries strongly depends on several factors including anode material, cathode material, ratio of capacity of anode to cathode, electrode binder, electrolyte solution and manufacturing process [1-8]. As a result, the rate of capacity fading of comparable lithium ion batteries from different manufacturers will not be the same. It has been reported, that the main reason is destruction of the SEI film, anode and cathode materials [1-2]. However, so far the disclosed data for the analysis were obtained based on products obtained from different manufacturers. As a result, a reliable comparison and further analysis could not be fully achieved.

In our laboratory, a pilot plant was assembled to manufacture lithium ion batteries. After optimization for 6 months lithium ion batteries with good cycling behavior, high capacity density and satisfactory safety were successfully prepared.

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without special requirements regarding room conditions such as humidity. As a result, a good basis to study capacity fading has been established in our laboratory. Our results on cathode materials show that there are evident changes of the cathode material LiCoO$_2$ $^9$. However, the cathode material contributed only a small partial capacity fading. Consequently, the changes of the anode material during long cycling were studied. Here we report results, which show that the crystal structure of the anode material is not evidently changed. However, its surface changes strongly, this process being mainly responsible for capacity fading of the lithium ion batteries.

**Experimental**

Lithium ion batteries were prepared as follows. The cathode material, LiCoO$_2$ and anode material (SSG, a modified natural graphite), graphitic carbon were home-made $^9$, polyvinylidene fluoride PVDF (Atofina 761) was used as binder, acetylene black as conductive additive. The cathode contained 90 wt.% LiCoO$_2$, 5 wt.% PVDF and 5 wt.% acetylene black, the anode 90 wt.% graphitic carbon, 5 wt.% PVDF and 5 wt.% acetylene black. N-methyl-pyrrolidone was used as solvent for the preparation of the electrode slurry. After coating on aluminum and copper foils, respectively, the cathode and anode were dried under vacuum. The dried foils were pressed to the required thickness and then cut according to the requirements of a prismatic cell 063450. Cathode and anode leads were welded by an ultrasonic welding machine. The welded foils of anode, cathode and a layer of separator (porous polypropylene Cellgard 2400 (Hoechst-Celanese, USA) were wound into a package and put into the Al gasket of the prismatic cell 063450. The lead of cathode was welded with the gasket and that of anode with the cover with a spot welding machine. Then the cover was welded to the Al gasket with a laser welding machine. After vacuum drying at 60 °C, the required amount of electrolyte solution (1 M LiPF$_6$ in ethylene carbonate, diethylene carbonate and dimethylene carbonate (1:1:1, weight ratio) LIB 315 from Guotai Huarong, China) was injected into the laser welded Al gasket through a small injection hole in the cover. Finally the hole was sealed with a steel ball. The prepared cells of type 063450 were used for the following measurements and analysis.

The formation process was done by charging at 0.2C to a cutoff voltage of 4.0 V. After storage for 7 days, four cells were taken out for measurement and analysis. The designed capacity of 063450 cells is 1000 mAh, and 3 cells (a, b and c) were cycled. The other one (a0) was used for control. The charging was at first galvanostatically performed at 1C rate to 4.2 V, the final voltage was fixed at 4.2 V. When the current dropped to 50 mA, the charging process was finished. After 5 minutes, the discharge process started at 1C rate to 3.0 V. After the discharge process, another rest of 5 minutes was observed, and then the charge and discharge process continued again. The three cells were stopped at 500, 1060 and 1600 cycles, respectively, then the cells were opened in an argon-filled glove box. The anode foils were washed with PC (propylene carbonate)/DMC(dimethyl carbonate) (1:1) solvent mixture prior to analysis.
The remaining capacity of graphitic carbon anode after different cycle numbers was measured as follows. Graphitic carbon material on one side of the washed anode was removed from the copper current collector. Then spherical pellets with diameter of about 1 cm were cut out from the copper foil with remaining carbon material. After drying and precise weighing, the cut pellets were put into an argon box and used as the working electrode and lithium metal as the counter and reference electrode to prepare model cells. The separator and electrolyte solution were the same as those used for the preparation of lithium ion batteries. The reversible capacity was galvanostatically measured at 0.1 mA/cm² in the range of 3.0 - 4.3 V.

Cyclic voltammograms were measured with the same cells with a CHI400 electrochemical analyzer between 2.0 - 0.0 V (vs. lithium metal) at a scan rate of 0.1 mV/s. Electrochemical impedance measurements (EIM, EG&G 5210) were performed in a two-electrode cell, whose electrodes were separated only by the above-mentioned film of the separator with the liquid electrolyte, at room temperature. The modulation voltage applied to the cells was 10 mV and the frequency range was between 100 kHz and 10 mHz.

X-ray diffraction patterns were recorded with an X-ray diffractometer (Bruker D8 Advance) with monochromatized Cu Kα radiation. The surface morphology was studied with a scanning electron microscope (SEM, Philips XL 300). X-ray photoelectron spectroscopy (XPS) was done with a PHI 5000C ESCA system.

Results and discussion

The cycling behavior of three 063450 cells is very good [9]. Their initial capacity is just several mAh higher than 1000 mAh, which agrees well with our design, they all present almost the same cycling behavior. At a capacity retention > 80%, the cycling number of our prepared cells is above 900. After extending cycling to 1600 cycles, the capacity retention is greater than 55 %, which shows that this kind of lithium ion battery will not fail suddenly. The curves also illustrate that the uniformity of the assembled cells is very good and the fading rate is almost the same. As a result, our preparation technique provides a good basis to analyze the capacity fading.

The remaining fraction of capacity of the graphitic anode after different cycle numbers measured by using lithium metal as counter and reference electrode and those of lithium ion batteries are shown in figure 1. The capacity of the anode material is just a little higher than the remaining capacity of the whole lithium ion battery. This indicates that the main reason for capacity fading is perhaps due to changes of the anode material. Of course, the cathode, LiCoO₂, also contributes to capacity fading of a lithium ion battery, which has been reported in our previous work and those of others [2, 9]. However, the influence of the cathode material on capacity fading is not very great since its crystal and surface structures are not changed very much.
Figure 1: Remaining capacity of graphitic anode (in percent) as a function of cycle number measured with lithium metal as counter and reference electrode, and remaining capacity of the lithium ion battery.

X-ray diffraction patterns of the anode prior to cycling and at 500, 1060 and 1600 cycles are shown in figure 2. There is almost no change of the peaks including both intensity and position. The minor change that can be identified is the change of the diffraction peak of the (006) plane. Prior to cycling, there is some evidence of this peak. After 500 cycles, it disappeared completely. This indicates that the crystal structure of the graphitic carbon does not change much during cycling. Consequently, the capacity fading must be ascribed to other factors.

Figure 2: X-ray diffraction patterns of graphitic anode after different cycles.

SEM micrographs of the anode prior to cycling and at 500, 1060 and 1600 cycles are shown in figure 3. After 500 cycles there is some visible change of the surface of the graphitic carbon particles and some white deposit can be clearly identified. With increasing number of cycles, the white deposits become more evident, indicating also the increase of the thickness of the surface film. On the surface of the cathode material, there are also white deposits growing with cycling. However, they
are much less evident\cite{9}. It was found that after storage for some time, the thickness of
the SEI film increases with storage temperature and time\cite{10}, and this is consistent with
our results.

![Figure 3: SEM micrographs of graphitic anode before and after different cycles.](image)

XPS data of all the elements at the surface of the anode material are measured
and partial results are shown in figure 4. The results show that the surface layer on the
graphitic anode after cycling comprises several compounds, in particular organic
compounds since the main constituents are carbon and oxygen since graphite is very
stable and the surface layer is different from the original one from graphite. In our
previous study of capacity fading, it was concluded that the surface deposits on the
graphite particles are composed mainly of lithium carbonate, lithium fluoride and
organic carbonates of lithium\cite{11}. This is consistent with the analysis of the surface
reported elsewhere\cite{1,14}. These deposited compounds result from the reactions of
electrolyte solution constituents with the graphite intercalation compounds of lithium,
Li_xC_6 (0 < x < 1), whose reactivity is much higher. During repeated cycling, they react
with the electrolyte and form a small amount of deposits. After extended cycling, the
deposits become evident observed from the above SEM micrograph. The relative
content (the total C-, O- and F-fraction of is 100%) of carbon decreases with cycling,
which is consistent with the increase in the thickness of the surface layer. The relative
content of oxygen increases with cycling. This is, of course, also due to the reactions
of Li$_x$C$_6$ with the electrolyte solution, which produce carbonates and/or polymeric carbonates [1, 12, 14]. The relative content of fluorine decreases with cycling. In the electrolyte solution are minor traces of water, even though the content is very small. However, we observed that the fluorides mainly deposit on the surface of the cathode due to the following reactions [9]:

$$\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiPOF}_4 + 2 \text{HF} \quad \cdots \quad (1)$$

$$\text{LiCoO}_2 + \text{HF} \rightarrow \text{LiF} + \text{HCoO}_2 \quad \cdots \quad (2)$$

If the produced HF reacts with the surface film components such as Li$_2$CO$_3$ on the anode, water will be formed again, and a fatal cycle will be established. Consequently, the lithium ion battery should not have been cycled so many times. As an alternative explanation of the decrease of fluorine content we suggest, that the fluorides are mainly from the reaction of the binder, PVDF, with Li$_x$C$_6$. With cycling and the formation of deposits, the amount of fluorides on the surface will decrease naturally.

**Figure 4:** Changes of the relative contents of carbon, oxygen and fluorine at the surface of the graphitic anode from X-ray photoelectron spectroscopy as a function of cycle number.

These results indicate that the SEI film results from the reactions of the electrolyte solution with the Li$_x$C$_6$ compounds during cycling. It was found that during the first 50 cycles, the production of gases from the reaction of the anode with the electrolyte solution is very strong. After 50 cycles, it is very small [15]. However, our results here show that even after 50 cycles or 500 cycles, the reaction still continues though it is very slow since the surface film increases with cycling after 500 cycles.

Figure 5 shows EIM data of the graphitic anode after different cycle numbers. They suggest, that the charge transfer resistance, which corresponds to the semicircle in the high frequency range, increases with cycling. This is consistent with the results of SEM and XPS discussed above, indicating the increase of the surface film. In the case of other graphitic anode materials, the charge transfer resistance also increases with cycling [16, 17]. When the charge depth is higher, the resistance also increases, indicating that capacity fading is partially due to the increase of resistance [18]. Perhaps the failure of conductive networks in the active graphitic carbon also contributes to the increase of the resistance [14].
Figure 5: Electrode impedance plots of the anode materials at different cycle numbers: (a) the original one and (b) the dilated one of the parts in high-frequency.

Cyclic voltammograms of the anode materials after different cycle numbers are shown in figure 6. The initially large current peak decreases after cycling due to formation of deposits and the increasing resistance, the inhibition becomes larger and the intercalation of lithium ions at a fixed potential is blocked [14]. However, the positions of the redox peaks do not change, which is consistent with the conclusion, that the graphitic structure evidently does not change as discussed above.

Figure 6: Cyclic voltammograms of graphitic anodes from lithium ion batteries at different cycle numbers, measured with lithium metal as counter and reference electrode at a scan rate of 0.1 mV/s.

These results show that the chemical compatibility of anode materials with the electrolyte solution is very important for good cycling behavior. For example, if the compatibility is very good, there will be no further reaction between them after the formation process. Consequently, good electrode material should have a very inert and stable surface structure [19, 20] and should not react with the electrolyte solution again after formation of the surface layer. This provides an important direction towards ways to achieve excellent cycling behavior of lithium ion batteries.
Conclusions

After 500, 1060 and 1600 cycles the internal graphitic structure of the anode material does not change significantly, and the major changes are only those of the surface film including its thickness and components. On the surface the amount of the deposits increases with cycling, and the main components also change. Due to the increase in the thickness of the surface film, the charge transfer resistance increases and the intensity of the cyclic voltammograms decreases with cycling. The capacity fraction of the anode material is just a little higher than that of the remaining capacity of the whole lithium ion battery. It is evident that the capacity fading is mainly due to the increase in the thickness of the surface film on the graphitic anode material. In order to achieve excellent cycling life of lithium ion batteries, the compatibility of the anode material with the electrolyte is very important.

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References