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The study of carbon half-cell voltage in lithium-ion secondary batteries

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Abstract

The half-cell voltage of carbon is measured by a three-electrode technique. In this study, the effects of cathode/anode mass ratio and charging patterns on the carbon half-cell voltages are investigated by factorial experimental design. From the results of analysis-of-variance (ANOVA), the top voltage of charge and the cathode/anode mass ratio are the major factors which influence the minimum half-cell voltage of carbon during charge. © 1997 Elsevier Science S.A.

Keywords: Factorial experimental design; Analysis-of-variance (ANOVA); Lithium-ion batteries

1. Introduction

Lithium-ion batteries are the most promising rechargeable batteries for portable electronic equipment. However, the safety issue is very important for batteries used in the consumer market. Although carbon instead of metallic lithium becomes a promising anode of lithium-ion batteries owning to its intercalation process only involving lithium ions. It is theoretically supposed that no metallic lithium will be detected during charge and discharge process. However, it has been experimentally shown that lithium will electrodeposite onto the carbon surface while the half-cell voltage of carbon reach the reduction potential of lithium. Electrodeposited lithium on the carbon surface may change the morphology of the electrode surface and the electrochemical behavior. Therefore, it is very important to prevent lithium deposition onto the carbon surface during charging.

To obtain high energy densities of rechargeable batteries with good cycle performance, the utilization of electrode materials should be as high as possible without lithium deposition onto the surface of carbon electrodes. However, to increase the utilization of electrode materials, both the anode and the cathode electrodes should be charged as fully as possible and, therefore, the possibility of lithium deposition will be increased. A careful design of the cell balance between anode and cathode materials as well as a proper charge pattern are key factors to design long cycle life of rechargeable batteries.

The purpose of this paper is to identify the factors which may potentially affect the possibility of lithium deposition. To prevent lithium deposition onto the carbon surface during charging, it is very important to keep the carbon half-cell voltage higher than 0 V (versus Li reference electrodes) which is the reduction potential of lithium. Thus, the minimum carbon half-cell voltage during charging may be an indication of the possibility of lithium deposition. The chance of lithium deposition onto surface carbon electrode will be increased as the minimum carbon half-cell voltage during charging being close to the reduction potential of lithium. To precisely estimate the importance of each control factor to the minimum voltage, analysis-of-variance (ANOVA) [1,2] was proceeded.

2. Experimental

High-purity graphite was used as the anode material with a 0.08 wt.% ash content, interlayer spacing $d_{002}=0.335$ nm and 10.0 m^2/g specific surface area (BET). The anodes were prepared by mixing 90 wt.% graphite powder with 10 wt.% polyvinylidene fluoride (PVDF) binder until a uniform slurry was obtained. The slurry was spread onto the copper foil to form the anode electrodes. The composition of cathode electrodes were 90 wt.% $LiCoO_2$, 6 wt.% acetylene black, and 4 wt.% PVDF binder. These cells are tested in a 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) + 1 M $LiPF_6$ electrolyte. The three-electrode cell with

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lithium as a reference electrode was used to monitor the half-cell voltage of each electrode and the whole-cell voltage.

A typical charge pattern of lithium-ion batteries is by a constant current charge first until the cell voltage reaching a setting voltage and followed by fixing the cell voltage at the setting voltage. The charge current will become fading instead of the constant current during the stage of constant voltage charge. Therefore, the percentage of charging current faded can be used to determine the end of charge. The setting voltage and the percentage of charging current faded at the end of charge are two important parameters for charging lithium-ion batteries.

Three control factors were selected in the experimental design, such as the top voltage of charge (V_{top}), cathode/anode mass ratio (C/A), and current drop percentage at the end of charge (I_{cut}). The top voltage of charge (V_{top}) is the setting voltage in the first charge stage. The current drop percentage at the end of charge (I_{cut}) is the percentage of charging current faded to cutoff charging. When the minimum voltage of carbon (V_{min}) is closer to the reduction potential of lithium deposition, the possibility of lithium deposition onto the surface carbon electrode will be increased. Therefore, the response of the experimental group is chosen as the minimum voltage of carbon (V_{min}) which is the hall-cell voltage of carbon electrodes at the end of charge. The cells were galvanostatically cycled at 0.6 mA/cm^2 to 4.1 V (or 4.2 V) top voltage for charge and to 2.8 V cutoff voltage for discharge.

3. Results and discussion

The overall-cell voltage and the half-cell voltage versus a reference electrode of lithium for both the anode and cathode during the first cycle measured in graphite/Li/$LiCoO_2$ cells are shown in Fig. 1. The minimum voltages of carbon (V_{min}), which are the half-cell voltages of the carbon electrodes at the end of charge, are 0.098 V (for V_{top} = 4.1 V) and 0.08 V (for V_{top} = 4.2 V). The V_{min} decreases as the top voltage of charge (V_{top}) increases. The measured minimum voltages of carbon (V_{min}) under various control factors are listed in Table 1. It is observed the minimum voltage are in a range of 0.076 to 0.122 mV. As the minimum voltage are more close to 0 V, the possibility of lithium deposition onto the carbon surface is increased. To precisely estimate the importance of each control factor to the minimum voltage, analysis-of-variance (ANOVA) was proceeded and the results are listed in Table 2. From the results of analysis-of-variance (ANOVA), it is observed that the top voltage of charge has a stronger effect on the minimum voltage than the other factors as well as their interactions. The F value shows a statistical confidence level by comparing the effect of each factor and their measuring errors, with a higher F value indicating the effect of the factor is much larger than measuring errors. The p-level shown in Table 2 is obtained from the corresponding F value, both F value and p-level tell the same thing but the p-level is a possibility level of making a mistake to believe the factor having a effect on the minimum voltage. It is statistically believed that the minimum voltage (V_{min}) is affected by the top voltage of charge (V_{top}) and the C/A ratio with a statistical confidence level of more than 99.9% Meanwhile, V_{min} is changed with the percentage of current drop at end of charge (I_{cut}) with 95% statistical confidence level. However, the effect of I_{cut} is only 0.038 mV, which is significantly smaller than that of the top voltage of charge (V_{top}). Interactions between these factors can be neglected owning to their minor effects on the minimum voltage of carbon electrodes with low statistical confidence levels. Higher top voltage of charge (V_{top}) and higher C/A ratio will get a lower voltage of carbon during charge, which will increase the possibility of lithium deposition onto the surface of carbon.

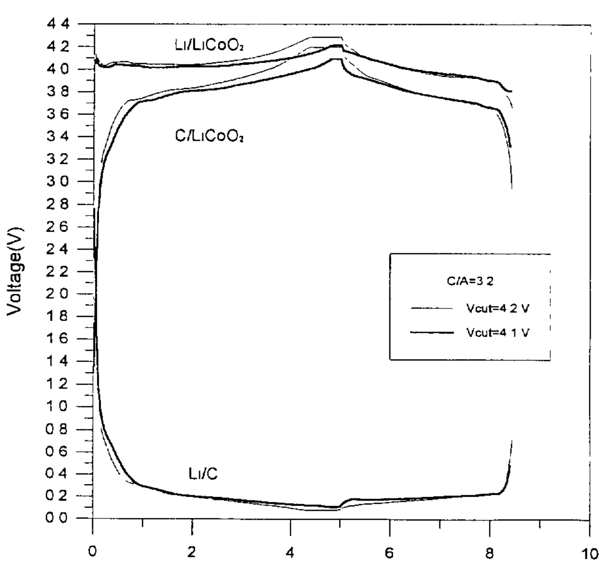

Fig. 1. Voltage profile of the three-electrode cells.

Table 1
Control factors and the minimum voltages (V_{min}) of carbon

Factors	V_{top} (V)	C/A ratio	I_{cut} (%)	V_{min} (V)
1	4.1	2.8	10	0.122
2	4.1	2.8	50	0.102
3	4.1	2.8	10	0.114
4	4.1	2.8	50	0.104
5	4.1	3.2	10	0.097
6	4.1	3 2	50	0.102
7	4.1	3.2	10	0.098
8	4.1	3.2	50	0.106
9	4.2	2.8	10	0 085
10	4.2	2.8	50	0.084
11	4.2	2.8	10	0.087
12	4.2	2.8	50	0.088
13	4.2	3.2	10	0.08
14	4.2	3.2	50	0.076
15	4.2	3.2	10	0.082
16	4.2	3.2	50	0.079

Table 2
Summary of analysis-of-variance for half-cell voltage of carbon

Factors		Effect		Error		F value [c]	p-level [d]
Symbol	Effects	df [a]	MS [b] (V)	df	MS (V)		
A	Top voltage of charge	1	0.021320	8	0.000007	291.349300	0.000000
B	C/A ratio	1	0.000267	8	0.000007	36.417200	0.000311
C	percentage of current drop	1	0.000038	8	0.000007	5.210400	0.051857
AB	interaction of A and B	1	0.000008	8	0.000007	1.090500	0.326880
AC	interaction of A and C	1	0.000007	8	0.000007	0.977800	0.351704
BC	interaction of B and C	1	0.000078	8	0.000007	10.642200	0.011489
ABC	interaction of A, B and C	1	0.000152	8	0.000007	20.757500	0.001860

[a] df: degree of freedom.
[b] MS: mean squares.
[c] F value: $MS_{effects}/MS_{error}$.
[d] p-level: results of F test.

4. Conclusions

The top voltage of charge (V_{top}) and the C/A ratio have a statistically significant contribution to the minimum voltage of carbon (V_{min}) with a more than 99.9% of statistical confidence levels. The minimum voltage of carbon decreases as the top voltage of charge (V_{top}) and the C/A ratio increased. The effect of the current drop percentage (I_{cut}) to the minimum voltage of carbon (V_{min}) is significantly smaller than that of the top voltage of charge (V_{top}).

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