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Aging experiments of $LiMn_2O_4$ battery and models for performance prediction

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Abstract

Various factors affect aging of lithium ion battery thus it's necessary to find out which factors have more influence and take this influence into the account of designing battery and BMS.

This paper aims to solve the problem by conducting aging experiments and then establish a semi-empirical aging model to predict usable capacity based on known mechanism and experiment data for BMS. At the first stage, ambient temperature, charge and discharge C-rate and cut off voltage for charging are considered. The experiment is conducted based on 20 pouch $LiMn_2O_4$ cells from MGL with a rated capacity of 5 Ah.

Keywords: lithium ion battery, aging experiment, performance prediction

1 Introduction

Performance degradation is one challenging problem stuck in the way of commercialization of power lithium battery. Aging due to cycle use is the most significant reason causing battery degradation.

Since the naissance of commercial $LiCoO_2$ battery in 1990s, the mechanism of aging has always been a popular topic among researchers. It is not understood thoroughly yet. Aging mechanism is so complicated that diversified side reactions inside the cell, for example, the formation of protective layer on anode and cathode surface, decomposition of electrolyte, corrosion of current collector etc can cause performance degradation[1-11].

Various external factors like ambient temperature, current, cut-off voltage for charging and discharging, working condition, mechanical vibration, shape of the cell(cylindrical or prismatic) and different internal factors like the cathode material, electrolyte material all have different effects on aging to some extent. It's necessary to find out which factors have more influence and take their influences into the account of designing BMS to make better use of lithium ion battery and to lengthen battery's lifetime. However, not sufficient research is performed.

In the past few years, there are sustained attentions on developing battery aging model for capacity or resistance prediction which can be divided into two separate groups according to their basis [12-21]. One group based on aging mechanism and the other group based on amounts of experiment data. It's difficult to tell which group is better for the aging mechanism is complicated and not understood thoroughly and experiment approach is essential to make up for the limitation.

This paper focuses on the topic of lithium ion battery aging and aims to find out which factors are severe by conducting long-term aging experiments and to establish a semi-empirical aging model containing these factors integrating some already known mechanism and experiment data.

Among all the factors affecting battery aging, depth of discharge(DOD) and cut-off voltage for discharging are excluded for their minute effect. Other factors will be taken into consideration, and under the current conditions of our lab, four factors: ambient temperature, charge and discharge current and cut-off voltage for charging will be studied at the first stage.

2 Experiment

2.1 Test profile

The experiment is conducted with 20 pouch $LiMn_2O_4$ cells manufactured by MGL with a rated capacity of 5 Ah. The value for each factor is listed in table 1.

Table 1: factor value

factors	value
Ambient temperature	20℃,50℃
Charge C-rate	C, 2C,3C
Discharge C-rate	1C, 2C,3C,4C,5C
Cut-off voltage for charging	4.2V, 4.35V, 4.5V

Ambient temperature is controlled through a temperature cabinet. Other factors are controlled through an 8-channel 5V/40A battery test system. At the first stage, 12 single factor tests were carried out according to the values in table 2. As in table 2, test 1 is a reference test with a standard test condition of 20℃, 1C discharge rate, 4.2V as cut-off voltage for charging and 1C charge rate. Test 2-12 are tests with one single factor different with test 1. As showed in table 2, blank means "same as test 1".

Table 2: single factor test

Test No.	T	Discharge current	Cut-off voltage	Charge current
1-1	20℃	C	4.2V	C
1-2		2C		
1-3		3C		
1-4		4C		
1-5		5C		
1-6		2.5C		
1-7		3.5C		
1-8				2C
1-9				3C
1-10	50℃			

Each cell is cycled for 500 times according to the predefined test profile as follows:

- Charge: the cell was charged with predefined charge current to predefined cut-off voltage in table 2 and then held at the voltage until the current dropped below 0.5A.
- Rest: the cell was rested for 20 minutes
- Discharge: the cell was discharged with predefined charge current until voltage dropped below cut-off voltage of 3.0V.
- Rest: the cell was rested for 20 minutes

2.2 Characterization

The test was interrupted for characterization every 50 cycles. The characterization tests include: (1) capacity test, (2) AC impedance test. All characterization tests are conducted at 20℃. Detailed test procedures are described as follows.

In the capacity test, the cell was fully charged with a 1C/4.2V CCCV (constant current and constant voltage) method until current dropped to 0.5A. After a 20 minutes rest, the cell was discharged to 3.0V. Then another 20 minutes rest follows. Three such cycles are performed and the average discharge capacity is defined as the usable capacity for the cell during aging.

In the AC impedance test, cell impedance at the frequency of 1000 Hz was measured for each cell at SOC=0.3 and SOC=0.7 with an equipment made by Hioki. The SOC here is defined based on the usable capacity updated by the capacity test not the rated capacity.

2.3 Cells screening

There is initial difference in capacity and impedance among fresh cells and this difference is often called inconsistency of cells. To exclude the influence of inconsistency on battery aging, cells must be screened before the aging experiment.

The screening process is based on the charging curves (figure 1 and figure 2) and discharging curves (not depicted) of the 20 cells. From the figures we can see that the charging curves of cells 3, 6, 12, 14 deviate from others which show that the four cells are not consistent with other cells. Thus other cells will be used in the aging experiment.

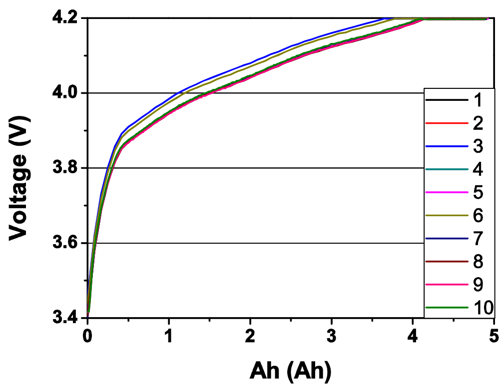

Figure 1: charging curves of cells 1-10

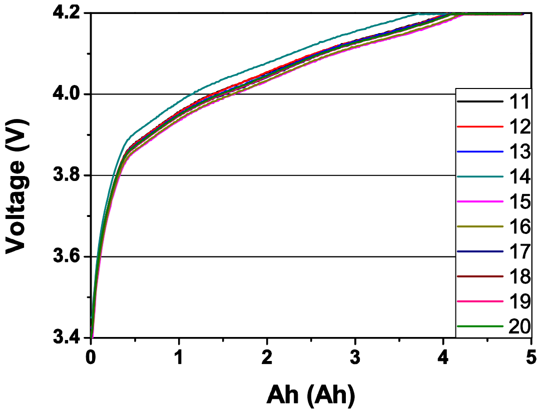

Figure 2: charging curves of cells 11-20

3 Results and discussion

The aging experiments last for six months. In order to examine the influence of discharge current, charge current, charge cut-off voltage and temperature on aging, we will plot the experiment results and make analysis below.

To make aging data comparable for batteries with different initial usable capacity, we define capacity degradation rate as follows, in which C_t refers to usable capacity after aging and C_0 refers to initial capacity.

$$\xi_c = 1 - \frac{C_t}{C_0} \tag{1}$$

Meanwhile, we use cumulative output capacity to replace time so as to decouple time and current. Thus, we can plot the capacity degradation under different conditions as figure 3,4,5,6 show. The results show that capacity decrease with time by a nonlinear manner. As early research shows, capacity decreases with time by a power pattern. Besides, the results show that degradation accelerates with an increase in current, charge cut-off voltage and temperature. In the following parts, we will analyze the influence of different factors respectively and establish aging model.

4 Aging model

4.1 Influence of temperature

Many former researchers have examined the influence of temperature and time on aging through experiments and modelling. Side reactions inside cells are the main reason causing degradation and it turns out that temperature accelerates degradation by affecting the speed of side reactions through an Arrhenius manner.

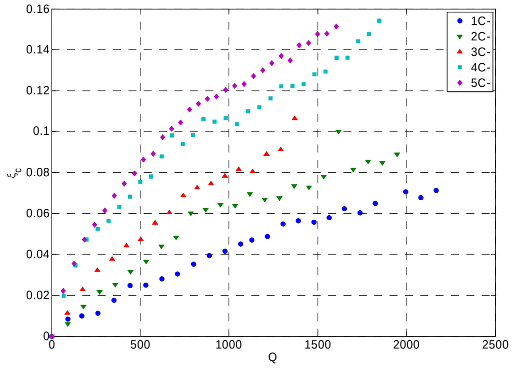

Figure 3: discharge current's influence on aging

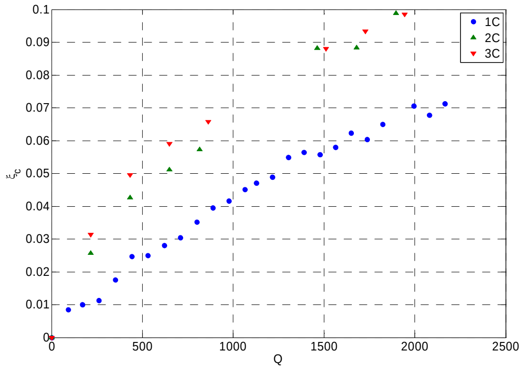

Figure 4: charge current's influence on aging

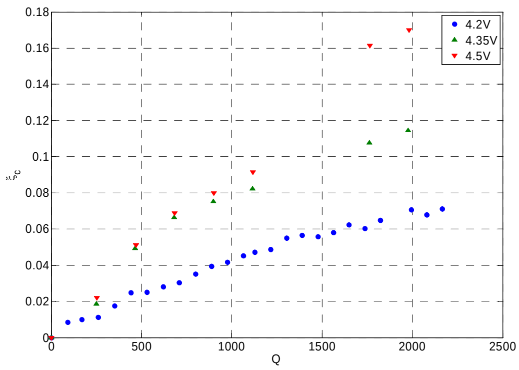

Figure 5: charge cut-off voltage's influence on aging

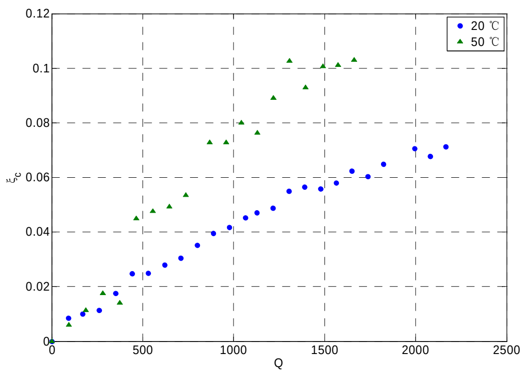

Figure 6: temperature's influence on aging

Thus, the capacity degradation rate can be expressed by the following equation

$$\xi_c = A\exp(-\frac{Ea}{RT}) \quad (2)$$

The logarithm form of equation (2) is

$$\ln \xi_c = -\frac{Ea}{R} \cdot \frac{1}{T} + \ln A \quad (3)$$

Clearly, the logarithm of ξ_c is linear with the reciprocal of temperature. With experiments data, we can calculate Ea=-16.2kj/mol, and plot the relationship in figure 7.

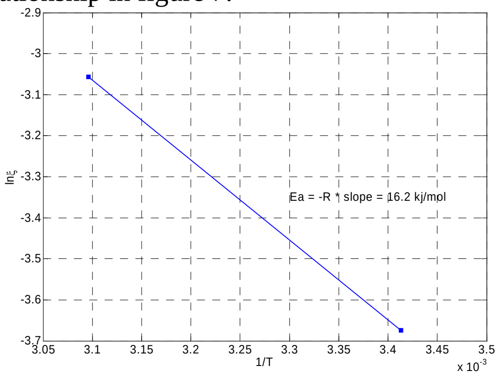

Figure 7: temperature's influence on aging

4.2 Influence of time

In former scientists' research, time influences degradation through a power manner, which can be denoted by equation (4), whose logarithm form is denoted by equation (5)

$$\xi_c = AQ^z \quad (4)$$

$$\ln \xi_c = z \ln Q + \ln A \quad (5)$$

Fitting equation (5) with aging data at 20 ℃, we find that when z =0.65 the goodness of fitting is best. Thus, we can rewrite equation (4) as follows, in which B denotes model error.

$$\xi_c = AQ^{0.65} + B \quad (6)$$

In equation (6), parameters A and B are related with battery's working condition, that is, current and voltage. We will discuss their influence next.

4.3 Influence of discharge current

Fitting equation (6) with aging data under discharge current of 1C, 2C, 3C, 4C and 5C, the values of parameters A and B and the goodness of fitting is showed in table 3.

Table 3: parameter value in model (6)

Discharge current	B	A	R^2
1C	-0.00405217	0.000522943	0.988259
2C	-0.00467681	0.000747456	0.954684
3C	-0.00206449	0.000916314	0.98764
4C	0.01313045	0.001031172	0.983698
5C	0.013518877	0.001183625	0.984123

By analyze values in table 3 we can find that discharge current affects parameter A in a linear manner while parameter B seems to be an random number.When discharge current equals 1C~3C ,the error B is approximately equal to 0, when discharge current equals 4C~4C, the error is equal to 1.3%. thus, we can rewrite equation(6) as follows, in which a_1 and a_2 denote the linear relationship between discharge current and parameter A. Model predicted value and experiment results are plotted in figure 8, in which we can see that the maximum estimate error is less than 2%.

$$\xi_c = (a_1 \cdot I_{dischar} + a_2)Q^{0.65} + B \quad (7)$$

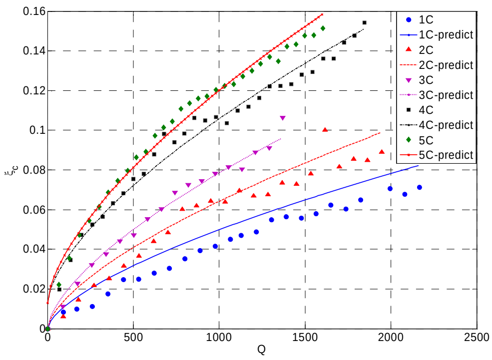

Figure 8: model predicted value and test value

4.4 Influence of charge current

As above, fitting equation (6) with aging data under charge current of 1C, 2C, 3C, the values of parameters A and B and the goodness of fitting is showed in table 4.

Table 4: parameter value in model (6)

Charge current	B	A	R^2
1C	-0.00405217	0.000522943	0.988259
2C	0.002066265	0.000720872	0.994296
3C	0.00734613	0.000693704	0.978775

By analyze the above value we can get similar conclusion. Charge current affects A in a linear form while error B is approximately equal to zero. Thus equation (6) can be rewrite as follows, and model predicted value and experiment results are plotted in figure 9, in which we can see that the maximum estimate error is less than 2%.

$$\xi_c = \left(b_1 \cdot I_{char} + b_2\right) \cdot \mathrm{Q}^{0.65} \qquad (8)$$

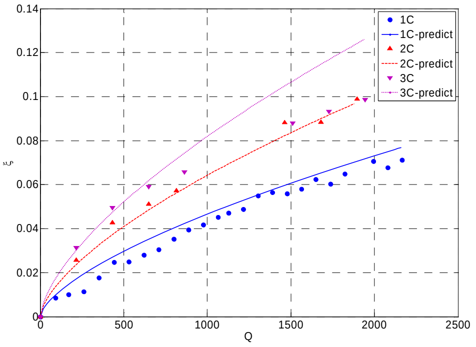

Figure 9: model predicted value and test value

4.5 Influence of charge cut-off voltage

As above, fitting equation (6) with aging data under charge cut-off voltage of 4.2V, 4.35V and 4.5V, the values of parameters A and B and the goodness of fitting is showed in table 5.

Table 5: parameter value in model (6)

Cut-off voltage	B	A	R^2
4.2C	-0.0040521	0.000522943	0.988259
4.35C	0.0041557	0.00081720	0.992341
4.5C	-0.0132114	0.00125254	0.961389

By analyze the above value we can get similar conclusion. Cut-off voltage affects A in a linear form while error B is approximately equal to zero when cut-off voltage is under 4.35V. Thus equation (6) can be rewrite as follows, and model predicted value and experiment results are plotted in figure 10, in which we can see that the maximum estimate error is less than 2%.

$$\xi = \left(c_1 V_{up} + c_2\right) \cdot \mathrm{Q}^{0.65} + B \qquad (9)$$

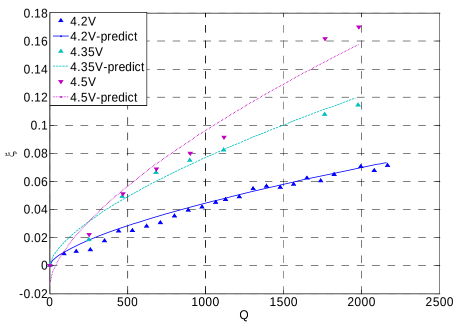

Figure 10: model predicted value and test value

4.6 Capacity degradation model

For equation (6), the value of parameter A and B are affected by charge/discharge current, charge cut-off voltage and temperature. It can be rewrite as following form

$$\xi_c = A(I_{dischar}, I_{char}, V_{up}, T)\mathrm{Q}^z + B(I_{dischar}, I_{char}, V_{up}, T) \qquad (10)$$

Thus, by substituting equation (2)(7)(8)(9) into equation(10), we can get the capacity degradation model

$$\xi_c == \left[0.53 \frac{(a_1 \cdot I_{dischar} + a_2)(b_1 \cdot I_{char} + b_2)(c_1 V_{up} + c_2)}{1000(a_1 + a_2)(b_1 + b_2)(4.2c_1 + c_2)} \cdot \mathrm{Q}^{0.65} + B\right] e^{-\frac{Ea}{293RT}(293-T)} \qquad (10)$$

5 Experiment verifying

To verifying the effectiveness of model (10), we conduct extra aging experiment. In the following parts, we will verify model (10) with different discharge current and longer aging time.

5.1 Different discharge current

Model (10) was established based on aging data of discharge current of 1C, 2C, 3C, 4C and 5C. To examine model's effectiveness, we conduct extra aging experiments under discharge current of 2.5C and 3.5C. The model predicted capacity degradation rate and test value are plotted in figure 11, in which we can see, the model error is less than 1%. It means the model can be well extended to other discharge current.

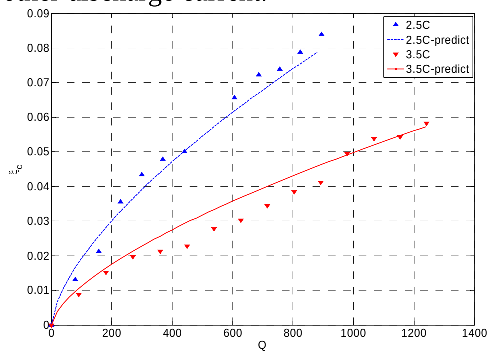

Figure 10: model predicted value and test value under discharge current of 2.5C and 3.5C

5.2 Longer aging time

Model (10) was established with experiment data of 500 aging cycle. To verify its effectiveness under longer aging time, we conduct aging experiment up to 600th aging cycle and plot the predicted value of all 600 cycle, as figure 11 shows. From the figure we can see that the model error is less than 1% after 600th cycle. It means the model can be extended to longer aging time.

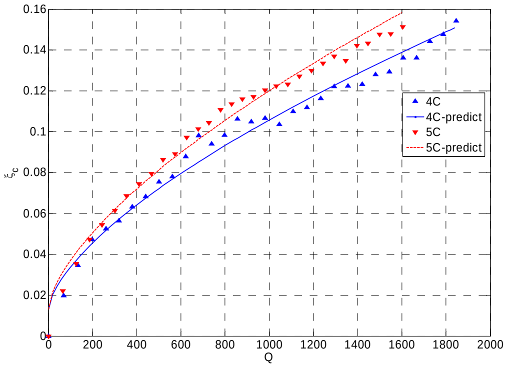

Figure 11: model predicted value and test value under longer aging time

6 Conclusion

In the paper, we analyze four key factors' influence on $LiMn_2O4$, conduct aging experiments on 12 pouch cells under different working conditions, establish an aging model which can be used to calculate battery's usable capacity during aging based on its working history, and in the end verify the effectiveness of the model through experiments. The results presented here are just the first part of our research. Next, we will improve our model to make it suitable for complex working condition so that it can be used in real vehicle's BMS.

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