Model of Battery Capacity Attenuation at Low Temperature

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Abstract. Lithium-ion batteries are widely applied for its advantages of being high in energy density, low in self-discharge rate, and high in maximal cycles, having no memory effect, and being pollutant-free. Accurately predicting the service lives of lithium-ion batteries is the important basis for reasonably working out battery replacement policy and ensuring safe use. For the purpose of this article, an acceleration model is devised for the valid period of capacity and the effect of temperature on lithium-ion batteries, revealing the pattern in the effects of capacity-related factors, and providing the fundamental data for the use of batteries at low temperatures.

1. Introduction
Motive power batteries serve as the core energy component of electric vehicles, and their development becomes the key factor in guiding the development of electric vehicles. The issue about examining the consistency among motive power batteries in a set during use has always been a major subject facing the further development in the industry of motive power batteries. Especially at a low temperature, a set of lithium-ion batteries connected part in serial and part in parallel will rapidly weaken, and the capacities of batteries will rapidly decay, far different from their original design values. Therefore, for the purpose of this article, at 20°C, -10°C, -20°C, and -30°C, the batteries with the same capacity, internal resistance, and initial open circuit are chosen, to separately combine into them two series batteries packs, which are discharged at 0.2C, with the voltage and temperature of each battery are monitored in real time [1-3]. As a result, a model of motive power battery capacity attenuation at low temperatures is made. The results of the study can provide technical assurance for supervision by relevant authorities, and offer technical guidance for the safe use of batteries in business.

According to already publicized studies, the causes of capacity attenuation include electrolyte oxidation-reduction, phase change of electrode during cyclic process, and continuous formation of Solid Electrolyte Interphase (SEI) film on cathode surface. Where, the continuous formation of SEI film is the main mechanism of attenuation for batteries in cyclic process at a higher C-rate. The oxidation-reduction reaction of solvent with lithium ions on cathode surface is the main reason for the growth of SEI film, and this reaction coincides with ion insertion/extraction when batteries are loaded. Ramadass et al. have proposed for the first time a multi-physical-field-based model of service lives for
lithium-ion batteries, and pointed out that the reduction reaction of solvent that occurs in the active carbon on cathode will occur constantly, so that SEI film will continue growing, and active lithium will be consumed continuously. Phoehn et al. and Safari et al. have developed a model of solvent diffusion to describe the formation and growth of SEI film on carbon cathode. Shi et al. have summarized in detail the phase-field model first in microscopic measure and then in mesoscopic measure, and after that, in macroscopic measure, the development in the study at home and abroad about the application of multi-scale simulation technology in the field of lithium batteries. Regarding the study about the electrochemical and thermal behavior inside a battery, simulation technology has advantages unmatched by any conventional research methods [4-8]. Furthermore, plenty of studies are concentrated on the effects of different working conditions on the maximal cycles for lithium batteries, as well as on how to accurately predict the service lives of lithium batteries. For numerous electrochemical models intended to pertinently deal with capacity attenuation, usually only the effects of heat generation and ambient temperature on the maximal cycles for batteries are taken into consideration, without combing the changes of parameters caused by the real-time change of temperature into the electrochemical models. Especially, there is no model of motive power battery capacity attenuation at low temperatures. Therefore, this article has intensively studied the model of motive power battery capacity attenuation at low temperatures.

2. Experiment
Let a lithium manganate motive power battery used in the test steadily go through 10 cycles: at a normal temperature (20±2), recharge the battery at a constant current of 3500 mA until a voltage of 4.2 V is reached, then recharge it at a constant voltage until a current of 350 mA is reached, set the time between recharge and discharge at 1h, and after that time passes by, discharge it at a constant current of 3500 mA until 2.7 V is reached. Repeat the above steps to complete 10 cycles of recharge and discharge, so that all the performances of the battery tend to be stable.

Let the battery stay for 6 h at the temperature in the test (e.g. -20℃ or -10℃), and then conduct the test on recharge at different temperatures.
Method of test: at the temperatures in the test (20℃, 0℃, -10℃, -15℃, -20℃, -25℃, and -30℃), use the system of recharge at constant current and voltage, and the system of discharge at constant current, that is, discharge the battery under test at a current of 3500 mA at the temperature in the test until the voltage of the battery reaches 2.7 V, put it in a still state for 1 h, then recharge it at a constant current of 0.5C until the voltage of the battery reaches 4.2 V before being recharged at a constant voltage, stop recharging it when the recharge current decreases to 350 mA, and repeat the cycle of recharge and discharge 10 times in this way, and monitor the voltage and temperature in real time. The test is as shown in Figure 1.
3. Model creation

Regarding lithium-ion batteries, generally, temperature and working current are considered to be the two major elements in accelerating battery capacity attenuation. The higher current the battery is discharged at, the faster its capacity is attenuated. At the same discharge current, the relationship between the maximal cycles for a lithium-ion battery and thermal effect generally complies with the acceleration model for the variables in acceleration.

\[ L = \frac{1}{K(T) \times I^C} \]  

Where, \( L \) is the valid period of capacity for the lithium-ion battery; \( I \) is the discharge current; \( K(T) \) is the function of temperatures; and \( C \) is a constant value.

At the same discharge current, let \( I = 1 \), the result is:

\[ K(T) = \frac{1}{L} \]  

(2)

As believed in general, the effect of temperature on the loss of a product’s effectiveness complies with this equation

\[ \frac{dM}{dt} = A_0 e^{\frac{-E}{kT}} \]  

(3)

Where, \( \frac{dM}{dt} \) is the rate of chemical reaction; \( M \) is a quantity representing modal characteristics; \( t \) is time; \( E \) is activation energy; \( K \) is boltzmann constant; \( T \) is absolute temperature; and \( A_0 \) is a constant.

\( M \), a quantity representing the modal characteristics of a lithium-ion battery, changes with time, becoming \( M_0 \) when \( t=0 \), and \( M_L \) when \( t=L \). If \( t=L \), the lithium-ion battery will lose effectiveness, and \( L \) is the service life of the lithium-ion battery in a certain chemical reaction. If temperature \( T \) is not related to time \( t \), and the amounts at both ends of the equation are integrated, and \( \Delta M = M_L - M_0 \) and \( L = tL - t_0 \) is a prerequisite, this equation will be obtained:

\[ \frac{dM}{dt} A_0 e^{\left(\frac{-E}{kT}\right)} \]  

(4)

On condition that the discharge current is unchangeable, the relationship between the lithium-ion battery’s service life \( L \) and the reciprocal of the temperature expressed in degrees is linear in the system of logarithmic coordinates.

When a lithium-ion battery is used at a low temperature, the polarization of lithium ions across the solid particles in anode and cathode will be enhanced significantly, resulting in incomplete discharge at final stage, and even total failure to supply power. Therefore, the loss of effectiveness at a low temperature is mainly reflected in that the persistence of battery capacity decreases with the decrease in temperature. See Table 1 for relevant model parameters for calculating capacity attenuation according to relevant inferences.

| Temperature/℃ | Temperature/°K | \( (1/T) / K-1 \) | Discharge capacity (mA·h) | Persistence of capacity \( P \) (relative to rated capacity) /% | \( \lg P \) |
|----------------|-----------------|------------------|-----------------------------|-------------------------------------------------|---------|
| 20             | 293             | 0.003413         | 12810                       | 96.61                                           | -0.0150 |
| 0              | 273             | 0.003663         | 11927                       | 83.21                                           | -0.0798 |
| -10            | 263             | 0.003802         | 11270                       | 67.09                                           | -0.1733 |
A drawing is made with the reciprocal of absolute temperature and the logarithm of capacity persistence in the system of rectangular coordinates, as shown in Figure 2.

It can be concluded from the result of fitting in Figure 2, the reciprocal of absolute temperature (1/T) and the logarithm of capacity persistence (lg P) maintain the following relations:

\[ \lg P = -23.44 + \frac{13354.03}{T} - \frac{1.90}{T^2} \]  

The fitness is 0.9863.

4. Conclusion
1) At the temperatures of -10°C, -20°C, and -30°C, the discharge capacity of the lithium-ion batteries in a set is equivalent to 88.0%, 82.5%, and 32.79% of its room-temperature discharge capacity respectively.

2) With the acceleration model, and in the light of Arrhenius equation, it is concluded that, the reciprocal of the absolute temperature and the logarithm of the capacity persistence maintain the quadric relationship in the temperature range of 20 - -30°C, at a fitness of 0.99.

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