PREDICTING THE LIFE OF LI-ION BATTERIES USING THE ARRHENIUS MODEL

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Abstract
The use of Lithium-ion (Li-ion) batteries has grown rapidly in a variety of fields, especially for long-term applications, which has made battery life prediction an important concern to be addressed. This paper presents the results of calendar aging tests performed on a small form factor Li-ion cell and the capacity degradation predictions that were made using the Arrhenius equation. The experiments were performed for one year at different temperatures and states of charge. The paper presents the results of the capacity degradation predictions during storage (calendar life) made by the Arrhenius equation and compares these predictions with actual capacity degradation observed over one year of testing. The paper also compares the variation in the capacity degradation predictions made using the Arrhenius equation for different test durations.

Introduction
The use of Li-ion batteries has expanded in the past few years from consumer electronic devices to a variety of other applications such as electric vehicles, telecommunication systems, backup storage for grid applications, etc. A number of these applications have significantly increased the requirements placed on the batteries and the environment that the batteries are expected to operate in. In addition, unlike consumer electronic devices, these applications require the batteries to continue operating for long periods of time, often exceeding 10 years. When selecting a Li-ion battery for an application that requires the battery to operate reliably for 10 years or longer, it is important to estimate the battery's performance given the operating conditions in the application. Selecting the wrong battery in these applications can result in expensive replacements as the batteries start to age prematurely and fail to meet the requirements of the application.

Performing real life aging studies on a battery is an expensive and time consuming task which may also be infeasible for some applications. Hence, over the years, many techniques and models have been proposed to estimate a Li-ion battery's life in an application. One study proposes the use of neural network simulations to model the aging of Li-ion batteries based on a change in the impedance of the batteries with time [1]. Other sophisticated quantitative models rely on using fish swarm algorithms [2] and Bayesian methods [3] to predict a Li-ion battery's performance in an application. A very popular technique for battery life prediction uses extrapolation of experimental data gathered by performing short term accelerated aging experiments to predict future performance of the battery in an application. The popularity of this technique is due to the simple accelerated aging experiments that are needed for predicting the battery's life in the application. Many different methodologies of accelerated aging and extrapolation of the accelerated aging data have been proposed in the literature. One such methodology relies on the Arrhenius equation which assumes that the capacity degradation of Li-ion cells during storage is predominantly temperature dependent. The methodology relies on predicting battery life based on accelerated aging tests that are typically performed for 12 to 16 weeks at different ambient temperatures.

This paper discusses the results of testing performed on a selected Li-ion cell model to make capacity loss predictions as a function of time and ambient temperature during storage (calendar life) using the Arrhenius model. The objective of the testing was to enable the prediction of capacity degradation for a variety of storage temperature and state of charge (SOC) conditions over a period of time.

Capacity Degradation

For Li-ion batteries with graphitic negative electrodes, one of the dominant degradation mechanisms involves the growth of the solid-electrolyte interphase (SEI) layer which increases the cell's impedance and reduces its capacity as it consumes cyclable lithium from the cell [8]. The ambient temperature at which a cell operates and/or is stored can have a large impact on the cell's capacity degradation. A high ambient temperature during storage coupled with a high SOC accelerates the rate of capacity degradation in a cell. The Arrhenius equation can be used to determine the impact of ambient temperature on calendar life. In order to evaluate the use of the Arrhenius model in predicting calendar life, a cell type was tested over a period of 52 weeks.

Calendar Aging

In the calendar aging tests performed, cells were stored at different temperatures and states of charge. Each test condition was performed with five cells to demonstrate the reproducibility of the experiment. The results show a similar aging for cells tested under the same conditions. As an example, the mean capacity loss at 60ºC for cells stored at different states of charge is as shown in Figure 1. The data indicates that as expected the cells experience an increasing capacity loss with a higher SOC and temperature.

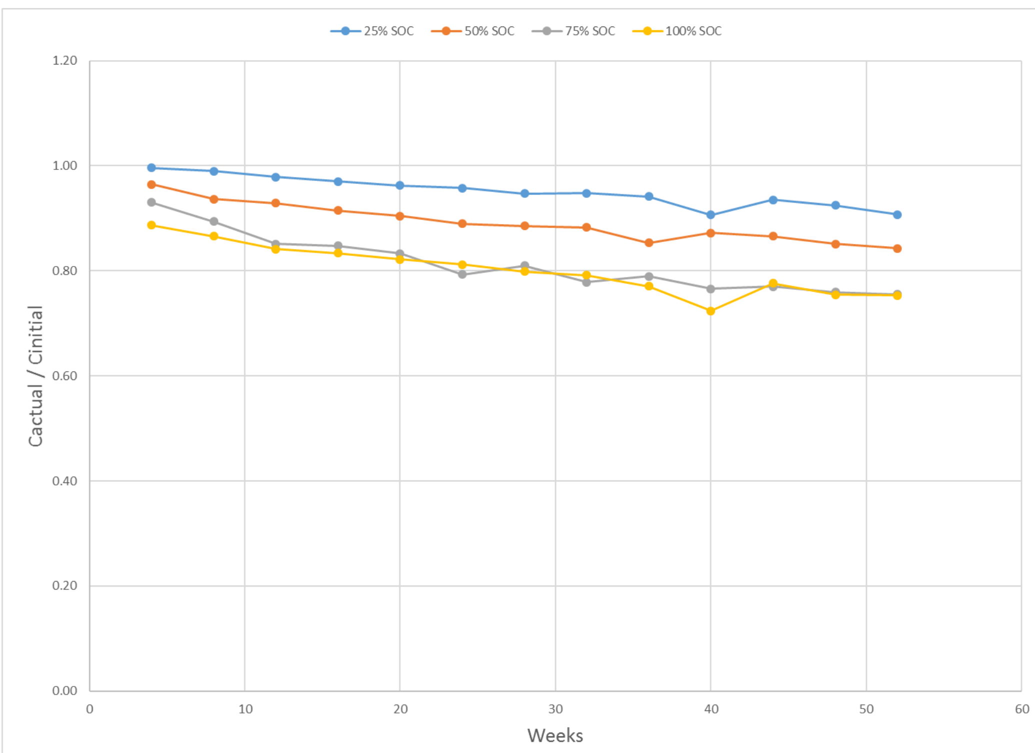

Figure 1. Normalized capacity over 52 weeks at 60ºC at different states of charge

Fit Method

The Arrhenius equation was used to obtain a lifetime model using the aging tests performed. The Arrhenius equation describes the relationship between the rate at which a reaction proceeds and its temperature. This equation is given as follows:

$$C_f = A * e^{\frac{-Ea}{RT}}$$

Where,

- C_f is the rate of change of some measured condition
- A is a dimensionless factor related to the probability that change in the measured condition will occur
- E_a is the activation energy required to change the measured condition
- R is the ideal gas constant
- T is temperature in Kelvin

Taking the natural logarithm of the Arrhenius equation yields:

$$\ln C_f = \left(\frac{-Ea}{R}\right) * \left(\frac{1}{T}\right) + \ln A$$

The capacity degradation at different temperatures (for a particular SOC) can be used to determine the activation energy (E_a) and the constant A by plotting the natural logarithm of the capacity degradation as a function of inverse temperature. As an example, Figure 2 shows the plot of the natural logarithm of the capacity degradation as a function of inverse temperature for a storage SOC of 75% and 100% for the tested cells.

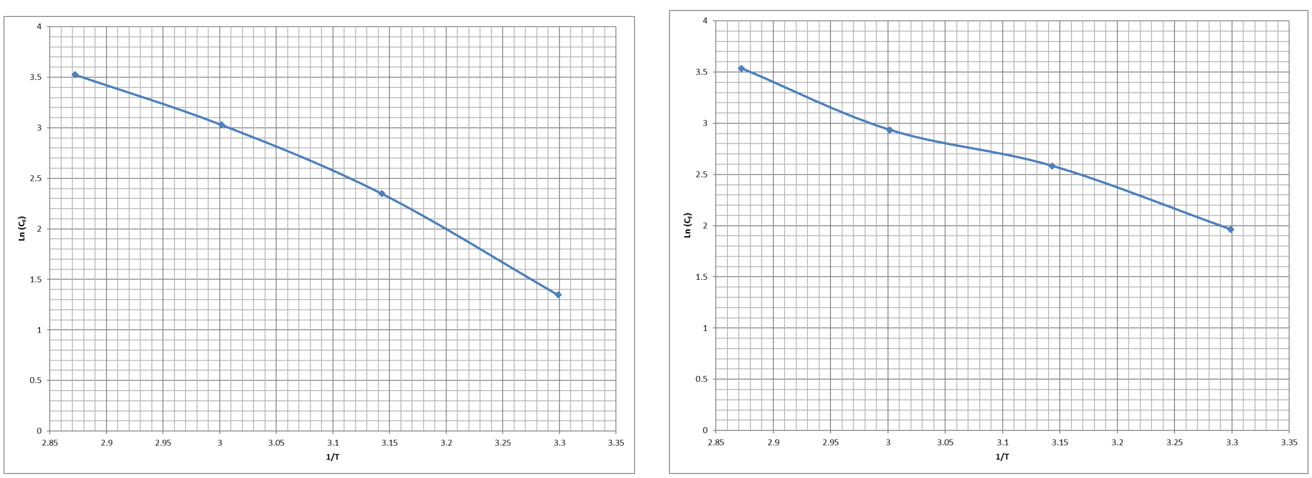

Figure 2. Capacity degradation as a function of temperature (75% SOC (left) and 100% SOC (right)) after 24 weeks of aging

As seen in Figure 2 the logarithm of the capacity degradation has an approximately linear dependency with the inverse temperature (r^2 value of 0.95 for 75% SOC and 0.97 at 100% SOC).

Time Dependence

For a Li-ion cell with a carbon-based anode, such as the one that was used for the experiments, the reviewed literature indicates that the dominant calendar aging effect is the formation of the SEI. The SEI is built up of decomposition products of the electrolyte, consuming lithium during formation and increasing resistance through the growing layer thickness. The literature indicates that although there are different theories on SEI formation, they all lead to a square root of time dependency [7]. This dependency was assumed in the model created to predict capacity degradation.

Calendar Aging Predictions

Once the activation energy and the constant (A) were determined, the square root of time dependency assumption was used to predict calendar aging for a particular SOC. The calendar aging experiments were performed for 52 weeks. As part of these tests, the cells were held at a set of different constant temperatures at various SOCs. Five cells were tested at each temperature/SOC combination. Capacity measurements were performed every four weeks at room temperature.

Figure 3 compares the predicted capacity degradation for a SOC of 75% with predictions made after 12 and 24 weeks of aging. The figure shows the capacity degradation predictions for approximately 3 years. Table 1 summarizes the capacity degradation predictions using data after 12 and 24 weeks of aging.

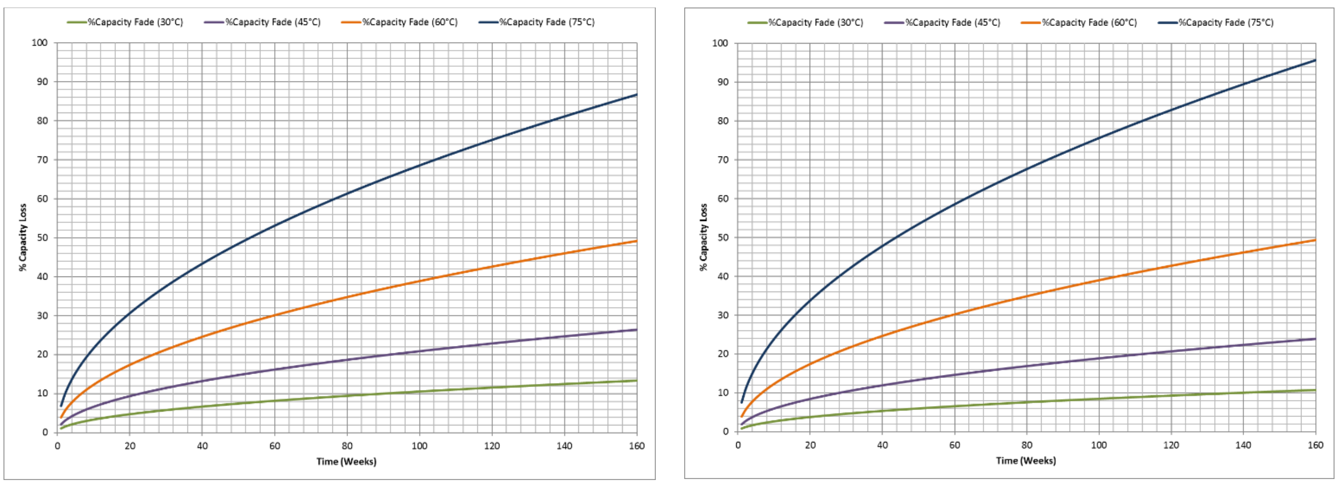

Figure 3. Predicted capacity degradation at approximately 3 years for 75% SOC, prediction made at 12 weeks (left) and 24 weeks (right)

Table 1. Predicted capacity degradation for aging performed for 12 weeks and 24 weeks at 75% SOC

	Predicted Capacity Degradation using 12 weeks of aging data				**Predicted Capacity Degradation using 24 weeks of aging data**			
	30ºC	**45ºC**	**60ºC**	**75ºC**	**30ºC**	**45ºC**	**60ºC**	**75ºC**
1 year	7.6%	15.1%	28%	49.5%	6.2%	13.6%	28.1%	54.5%
2 year	10.8%	21.3%	39.6%	69.9%	8.6%	19.1%	39.4%	76.4%
3 year	13.2%	26.1%	48.5%	85.7%	10.7%	23.6%	48.7%	94.5%

Figure 4 shows the predicted and actual capacity degradation using data after 12 and 24 weeks of aging for a SOC of 75%. Figure 5 shows the capacity degradation predictions for a SOC of 100%.

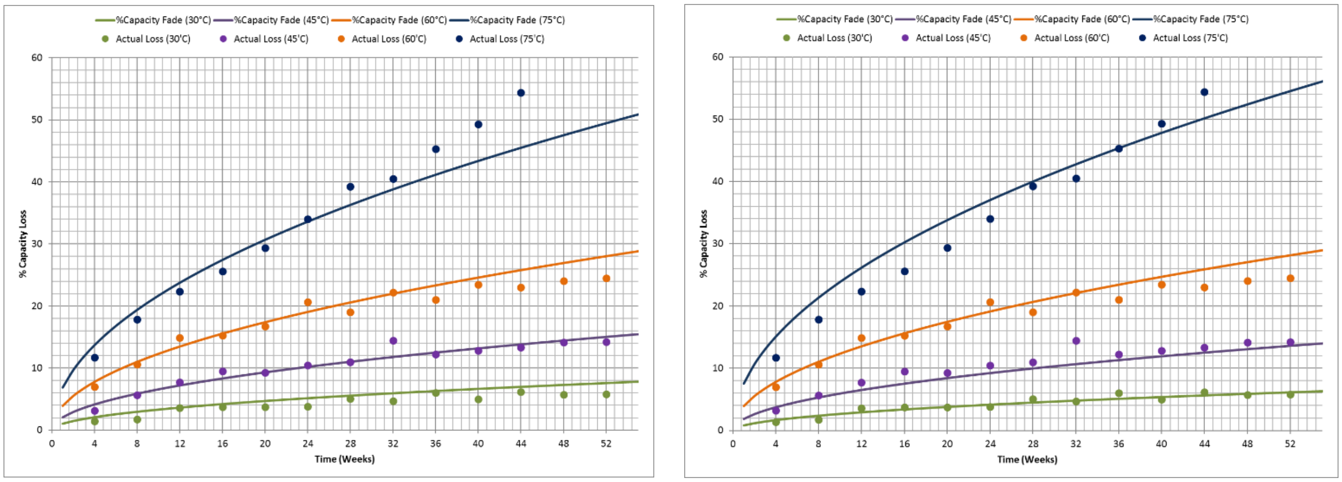

Figure 4. Actual capacity degradation vs. predicted capacity degradation using 12 weeks (left) and 24 weeks (right) of aging data at 75% SOC

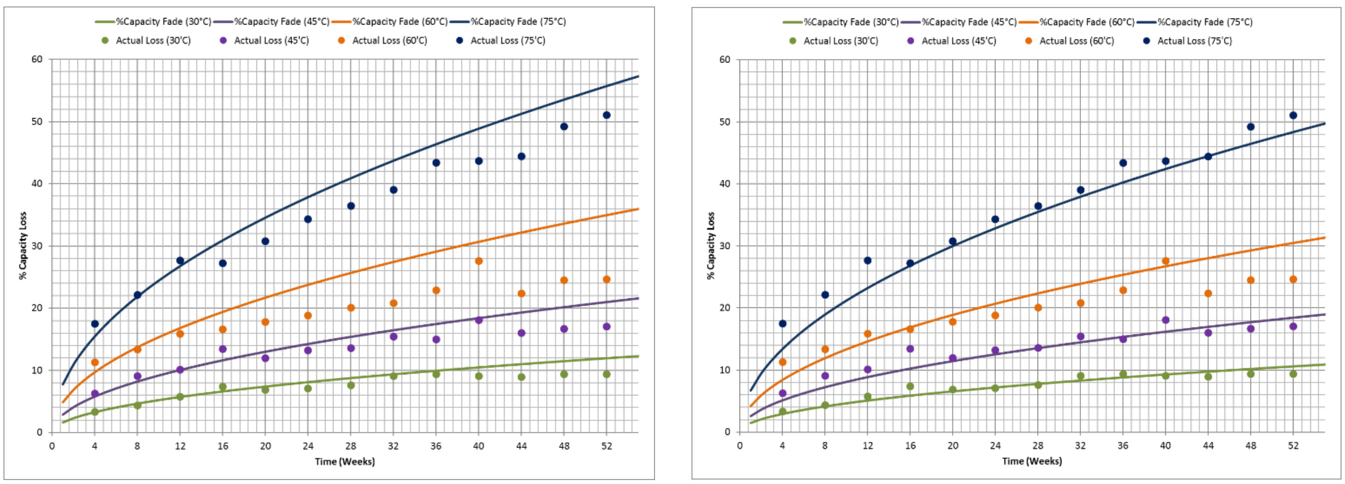

Figure 5. Actual capacity degradation vs. predicted capacity degradation using 12 weeks (left) and 24 weeks (right) of aging data at 100% SOC

Table 2 summarizes the results of the capacity degradation predictions and the actual capacity degradations measured during the 52-week aging test. The data indicates a similar accuracy when capacity degradation predictions are made using data after 12 weeks and 24 weeks of aging.

Table 2. Measured capacity degradation vs. predicted capacity degradation at 52 weeks for aging performed for 12 weeks and 24 weeks at 75% SOC

	Measured Capacity Degradation	Predicted Capacity Degradation using 12 weeks of aging data	Predicted Capacity Degradation using 24 weeks of aging data
30ºC	5.8%	7.6%	6.2%
45ºC	14.3%	15.1%	13.6%
60ºC	24.5%	28.0%	28.1%

Summary

The Arrhenius equation was used to predict the calendar aging of a selected Li-ion cell. The predictions made using the Arrhenius equation after both 12 and 24 weeks of aging were compared with actual capacity degradation observed over 52 weeks of testing. The acquired data and the developed capacity loss model predicts a reduction in the rate of capacity loss as a function of time. In addition, the testing performed indicates that the capacity degradation predictions for the tested cells made using the Arrhenius model are similar for both predictions made after 12 weeks of aging and 24 weeks of aging for ambient temperatures up to 60ºC.

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