

The correlation between the capacity fade of LiFePO_4 batteries and cycle life

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Abstract

A new model is developed by fitting the capacity of LiFePO_4 batteries, which can be used to investigate the relationship between capacity fade, state of health (SoH), electrochemical reactions and the number of cycles. The equation for the proposed model based on modified Thevenin circuit, Butler-Volmer kinetics and regression analysis consists of a constant term, a sine-exponential term and an exponential term. The constant term represents the rated capacity of a battery, while the sine-exponential term represents the variation in capacity in the active status and the exponential term represents the variation in capacity in the stable status. The model is divided into two parts. The first part is represented by the sine-exponential term, responsive to the activation of electrolyte and electrodes in the first 180 cycles; the second part can be described by the exponential term, estimating

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the capacity from cycle 180 to cycle 2000. In addition, the comparison between the model and mean absolute percentage error (MAPE) is able to predict the serious decay of capacity. The MAPE is only 0.47% for the tested battery. The proposed model also successfully estimates the capacity of a tested battery where the number of cycles is 2000 with the error of 0.90%. The results mean that the model is able to closely describe the correlation between capacity and the cycle numbers.

1 Introduction

LiFePO₄ batteries are widely used as energy sources in 3C (Computer, Communication and Consumer Electronics) products, photovoltaic system, electric vehicles (EV) and smart grid applications [1, 2, 3]. Thanks to their higher energy conversion efficiency, longer lifetime, higher safety, and reliability, the LiFePO₄ battery represents the best solution for providing high energy densities for the operational needs of many power products [4]. Though the LiFePO₄ battery has many advantages, it still has an innate problem - the potential for capacity fades as the number of cycles increases.

The capacity fade reflects the health condition of a battery and its ability to deliver the power to load. In general, the state of health (SoH) is obtained by comparing the current capacity with the rated capacity of a battery. However, it is still not easy to determine SoH [5]. Hence, many research studies about SoH and state of charge (SoC) for Lithium-ion battery elucidate that an accurate model is crucial for the estimation of the cycle life and SoH of a battery [6]. However, it is important to understand the characteristics and electrochemical reactions of the LiFePO₄ battery for developing the model.

Since aging of the materials occurs inside the battery, it is not easy to accurately investigate the relationship between the capacity and the charge-discharge cycle. A variety of battery models are developed to capture the battery characteristics [7, 8]. The above studies are good for estimating the SoH and understanding the reasons of performance degradation of a battery.

However, if a model has a lot of difficult settings and complicated parameters, it may spend more times on computing and have the worse computational efficiency. Therefore, the parameters of the model must be as simple as possible.

In EMAC 2013 [9], the relationship between voltage variation and SoC was investigated and a mathematical model was developed, particularly for batteries in different conditions; in EMAC 2015 [10], the relationship between capacity fade and cycle number was investigated and a mathematical model was developed as well; However, the model cannot estimate the capacity variation of a LiFePO_4 battery at around the first 180 cycles because the capacity varies obviously due to the activation of the electrochemical reaction inside a LiFePO_4 battery. Therefore, a new model is proposed to fully describe the capacity variation of a LiFePO_4 battery in this paper, particularly for the beginning period (around the first 180 cycles of the cycle life) of a LiFePO_4 battery.

The equation of the proposed model contains a constant term, a sine-exponential term, and an exponential term. The constant term represents the rated capacity of a battery. The sine-exponential and exponential terms represent the variation in capacity, which strongly depends on the activation process of the electrode, the solid-electrolyte interphase (SEI) formation, the fatigue and fracture of the graphite lattice, and the consumption of lithium, etc. The proposed model is able to closely describe the correlation between capacity and cycle number.

2 Model development

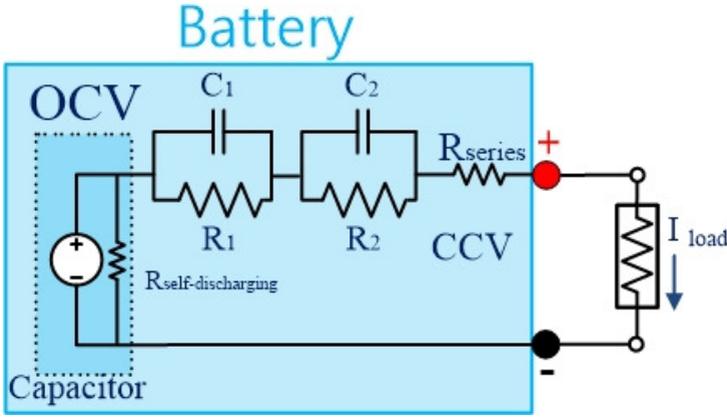


Figure 1: The electrical circuit model for a LiFePO_4 battery.

2.1 Model derived from modified Thevenin circuit, Butler-Volmer kinetics and regression analysis

This study was conducted in order to observe the variation in capacity as the number of cycles increases, and then to develop a new model derived from the electrical circuit model and Butler-Volmer kinetics to analyse the battery status. The modified Thevenin circuit model is composed of an open-circuit voltage (OCV) source, a series resistor (R_{series}) and two resistor-capacitor (RC) circuits as shown in Figure 1 [10, 11]. RC circuits are used to investigate both charge and discharge behaviours of the battery.

When a battery is connected to a load, the capacitors in the RC circuits are charged and the voltages across the resistors are increased, leading to the reduction of closed-circuit voltage (CCV). When the battery is disconnected from a load, the capacitors in the RC circuits are discharged by the parallel resistors and the voltages across the RC circuits decrease. Therefore, the measured voltage gradually recovers from a CCV level to an OCV level. From the circuit theory, the charge and discharge behaviours of two RC circuits can be represented by two exponential terms.

As the variations of voltage and current density of a battery obey Butler-Volmer kinetics, the proposed model can be derived from Butler-Volmer kinetics as well. Butler-Volmer kinetics describes the electrochemical reaction that takes place within a LiFePO₄ battery, and is expressed as [12, 13].

$$i = i_0 \cdot \left\{ \exp\left(\frac{\alpha n F \eta}{RT}\right) - \exp\left(\frac{(\alpha - 1)n F \eta}{RT}\right) \right\}, \quad (1)$$

where i is the electrode current density (A/m²), i_0 is the exchange current density (A/m²), η is the surface overpotential (V), T is the absolute temperature (K), n is the number of electrons involved in the electrode reaction, F is the Faraday constant, R is the universal gas constant, α is the anodic charge transfer coefficient, and $(\alpha-1)$ is the cathodic charge transfer coefficient. In a battery, α is usually assumed to be 0.5 [14, 15].

The surface over-potential, $\eta = (E - E_{rev})$ where E is the difference between the mean electrostatic potentials of ions and electrons (V), E_{rev} is the Nernst equilibrium potential (V), which is strongly related to the local activity of lithium [12, 16]. According to Faraday's Law, the capacitance is the integral of the current over time. Therefore, the battery capacity is written as:

$$\text{Capacity} = \int_{t_0}^{t_1} i_0 \cdot \left\{ \exp\left(\frac{\alpha n F \eta}{RT}\right) - \exp\left(\frac{(\alpha - 1)n F \eta}{RT}\right) \right\} dt, \quad (2)$$

where t_0 is the start time of the discharge process, and t_1 is the end time of the discharge process.

Since the tested battery was discharged using a constant current, the capacity is proportional to the double exponential equation. Therefore, the proposed model can have two exponential terms which are suitable for the representation of the equivalent circuit in Figure 2 and Butler-Volmer kinetics. The proposed model expressed below consists of a constant term, a sine-exponential term, and an exponential term, and was developed to closely fit the capacity curve so that the proposed model can be used to analyse the capacity of a LiFePO₄

battery.

$$\text{Capacity}(m) = r - \sin\left(\frac{2\pi}{\lambda} \cdot m\right) \cdot a_1 \cdot e^{(b_1 \cdot m)} - a_2 \cdot e^{(b_2 \cdot m)}, \quad (3)$$

where m is the number of cycles. The parameters r , a_1 , λ , b_1 , a_2 and b_2 are obtained following the curve fitting.

Since the equation is derived from the electrical circuit model shown in Figure 1 and electrochemical reaction from the Butler-Volmer kinetics, there will be four parameters for the two exponentials. In addition, the rated capacity of the tested battery may be different so that there will be a parameter for the rated capacity of a tested battery. Once the tested battery is different, the shape of the curve in the active zone (the beginning period of the cycle life) may be different so that there will be a parameter for the shape of the active zone as shown in Figure 2. Therefore, there will be six parameters for the proposed equation.

The measured capacity curve versus the different number of cycles and the fitting curve (dashed line) are plotted in Figure 2, along with the asymptote of the measured curve (dotted line). It can be observed that the measured curve contains two different characteristics, where the first one is termed as the active zone, and the second one is termed as the stable zone. As the LiFePO_4 battery is very stable and it is capable of being cycled over 2000 times.

In Equation (3), r is a constant term that represents a rated capacity of 15000 mAh, a_1 and a_2 determine the initial capacity of the battery when m is zero and also decide the position of the turning point, i.e., the intersection between the measured curve and the asymptote. The units of a_1 and a_2 are mAh. The term $\frac{2\pi}{\lambda}$ determines the shape of the capacity in the active zone, where the unit is 1/number. The value of b_1 determines the change in capacity of a battery within the active zone, where the unit is 1/number. The value of b_2 determines the capacity decay rate in the stable zone, where the unit is 1/number.

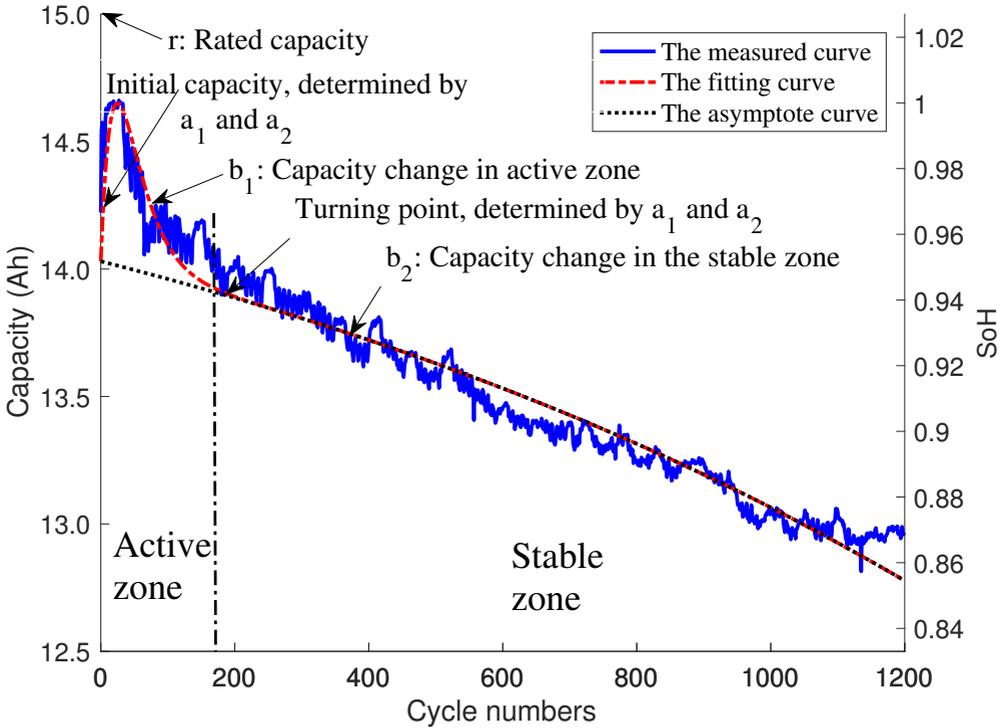


Figure 2: The measured capacity curve versus the number of cycles, together with the asymptote of the measured curve (dotted line) and the fitting curve (dashed line).

Table 1: The parameters for the proposed mathematical model

Parameter	r	α_1	λ	b_1	α_2	b_2
Values	$1.5 \cdot 10^4$	$2.362 \cdot 10^5$	$-2.188 \cdot 10^4$	$-3.922 \cdot 10^{-2}$	$9.695 \cdot 10^2$	$7.1 \cdot 10^{-4}$

2.2 Experimental procedure

The rated capacity of the power batteries being tested is 15Ah, and the working voltage is 3.2 V. The cut-off discharging voltage was set at 2.0 V, and the upper bound of the charging voltage was set at 3.65 V. Each LiFePO_4 battery was charged until the voltage reached 3.65 V using a direct current (DC) power source based on the constant-current and constant-voltage (CC-CV) method. The batteries were tested at a constant temperature in an air-conditioned laboratory. The batteries were then left idle for a certain period to ensure that the voltage barely varied. The batteries were then discharged using a DC electronic load at a discharging current of 1 C rate based on the constant-current mode until the voltage reduced to the cut-off discharging level of 2.0 V. 1 C rate is defined as the discharging current that completely discharges the nominal capacity of a battery in one hour. Therefore, in this research, the discharging current is 15 A. The data was automatically recorded and analysed by the computer. The tested batteries were cyclically charged and discharged 1200 times. Hence, the relationship between the variation in capacity and the number of cycles can be determined. The process flow for the experiment is illustrated in Figure 3.

3 Results and discussion

The MATLAB program was used to analyse the curve for the measured capacity versus number of cycles and the fitting curve. The obtained values for parameters r , α_1 , λ , b_1 , α_2 and b_2 are summarised in Table 1.

Equation (3) is used to represent the three different reactions that take place in

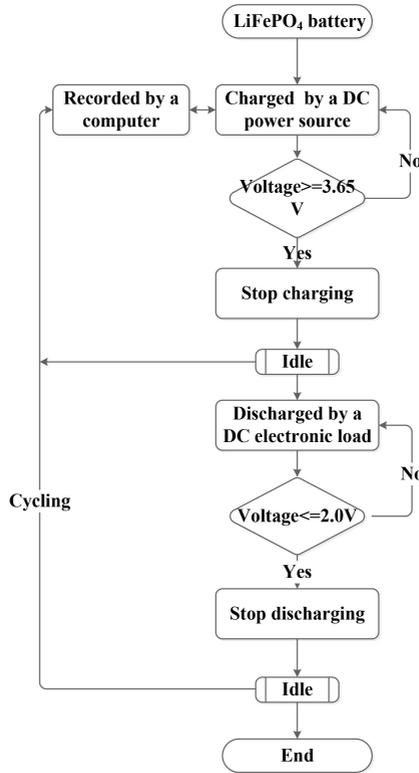


Figure 3: Experimental flow.

a battery. First, the electrodes are activated during the charge-discharge process because the contact between the particles on the electrodes and electrolyte causes the electrodes to expand and contract due to a phenomenon called the swelling effect [17], meaning that the transmission of Li^+ is improved and the active area for the electrochemical reaction is also increased. Consequently, both the charge transfer resistance on the surface of the electrodes and the mass transfer resistance of the electrodes is decreased. The capacity of a battery rapidly increases in a short period (about 30 cycles), as shown in Figure 2. As the swelling effect becomes worse, the materials comprising the electrode and the electrolyte begin to decay, generating impediments such

as the formation of a thicker SEI and a slower diffusion rate of Li^+ ions, causing the capacity to rapidly decrease at around 30 to 180 cycles. Hence, the capacity in the zone (0-180 cycles) which we call the active zone is very active, and is dominated by the $\sin(\frac{2\pi}{\lambda} \cdot m) \cdot \alpha_1 \cdot e^{(b_1 \cdot m)}$ term of Equation (3). It can be observed that this fitting curve only changes significantly when the number of cycles is less than 180.

Subsequently, the battery capacity gradually fades, since the slow thickening of the SEI layer continues to consume the cyclic lithium during the cycling process and the electrode material also slowly decays, although this reaction is relatively mild for a battery. Therefore, the phenomenon occurs in the zone which we call the stable zone and the $\alpha_2 \cdot e^{(b_2 \cdot m)}$ term of Equation (3) is dominant. r term of Equation (3) represents the rated capacity of the battery. Finally, by combining the three terms, Equation (3) can demonstrate the change in capacity of a battery from 0 to 1200 cycles. Therefore, α_1 and α_2 will determine the initial capacity in the beginning period, and b_2 will determine the rate of decay of the capacity in the stable zone.

The accuracy of the proposed model for the tested batteries is investigated by using the mean absolute percentage error (MAPE) between the experimental data and the fitting data. The MAPE equation is expressed as

$$\text{MAPE} = \frac{1}{p} \sum_{p=1}^{1200} \frac{|c_{\text{exp}} - c_{\text{fit}}|}{c_{\text{exp}}} \cdot 100\%, \quad (4)$$

where c_{exp} denotes the experimental data, c_{fit} denotes the fitting data, and p is the number of the recorded data.

The results for the tested battery indicate that the MAPE value is less than 0.47%. The error between the experimental and the fitting data for each cycle is also shown in Figure 4, where it can be seen that the maximum error is about 3.08% and is located in cycle 2. It can also be seen that the higher values of errors occur at around the start point (0-30 cycles), the turning point (150-180 cycles), and the end point (1170-1200 cycles). This is because that

Table 2: The MAPE, the maximum error, minimum error, and the error at cycle 2000 for a tested battery.

Symbols	Values
MAPE (%)	0.47%
Maximum error (%)	3.08%
Minimum error (%)	$3.97 \cdot 10^{-4}\%$
Error at cycle 2000 (%)	0.90%

these three points are the boundaries of the different electrochemical reactions or the boundaries of the different electrical characteristics so that the fitting is not easy. Furthermore, the proposed model can be extended to perform an estimation of the capacity fade beyond 1200 cycles. When comparing the measured capacity value of a tested battery with the estimated value from the proposed model at cycle 2000, the error is only 0.90%, as shown in Table 2 and Figure 5. This indicates that the battery capacity corresponding to the number of cycles is closely estimated using the proposed model.

The proposed model can also be used to estimate the SoH of the tested battery, as indicated by the vertical axis on the right-hand side of Figures 2 and 5. In order to increase the accuracy of the estimation of SoH, the maximum measured value of the capacity (about 14.6 Ah) is used to replace the rated capacity (15 Ah) and the measured capacity at each cycle can be replaced by the developed equation (Equation (3)). The modified equation for calculating the SoH is expressed as

$$\text{SoH} = \left| \frac{C_{\text{exp}}}{C_{M\text{exp}}} \right|, \quad (5)$$

where $C_{M\text{exp}}$ is the maximum value from the experimental data and C_{exp} is the measured value of the capacity.

It can be seen that the SoH reduces to about 0.88 and 0.75 at cycle 1200 and cycle 2000, respectively. If the real initial capacity value (14.0 Ah) is used in the regularization purposes, the SoH values for each cycle will be higher.

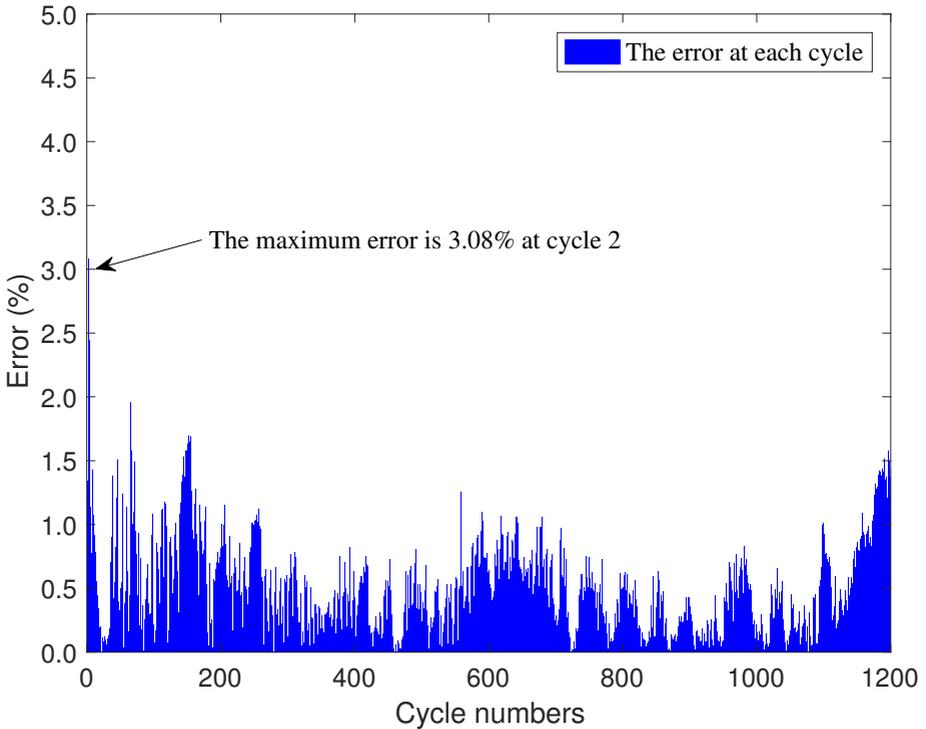


Figure 4: The absolute percentage error at each cycle for a tested battery

4 Conclusions

In this study, a new model derived from modified Thevenin circuit, Butler-Volmer kinetics and regression analysis is developed in order to investigate the capacity fade of a LiFePO_4 battery. Consequently, the proposed model is composed of a constant term, a sine-exponential term, and an exponential term. The constant term represents the rated capacity of the battery; the sine-exponential term dominantly represents the capacity in the active zone and the exponential term represents the capacity in the stable zone. The

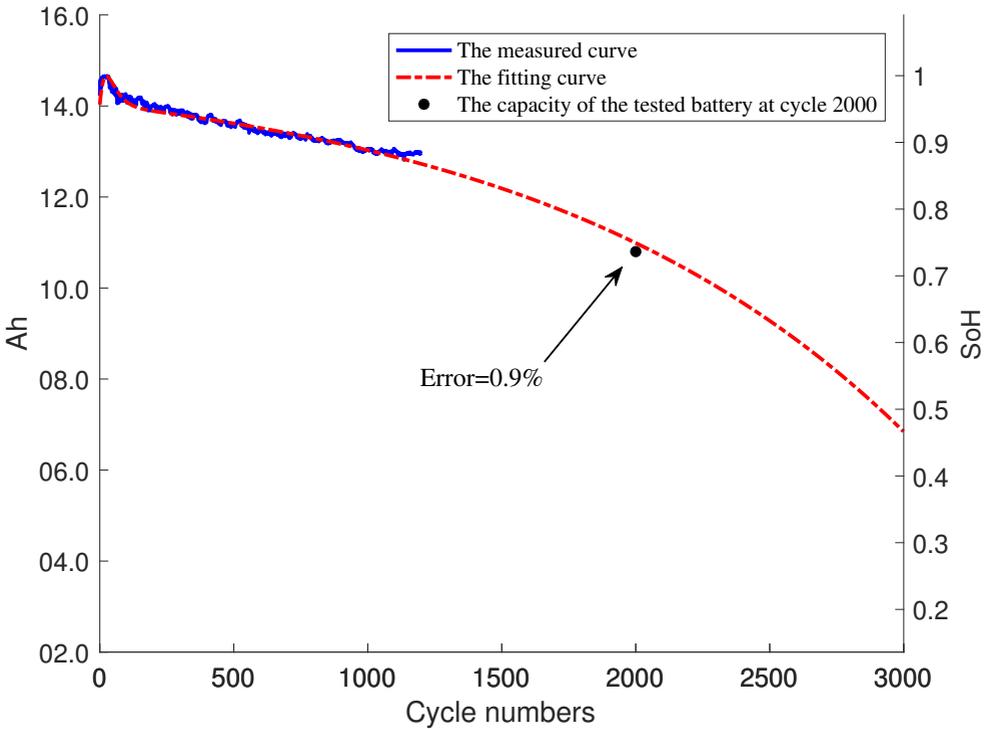


Figure 5: The absolute percentage error at each cycle for a tested battery

MAPE is only 0.47%. In addition, the model also successfully estimates the capacity of a tested battery where the number of cycles is 2000 with the error of 0.90%. Based on this trend, the proposed model can be used to estimate the health conditions of a battery as well.

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