Intelligent Lithium-Ion Battery State of Charge (SOC) Estimation Methods

Intelligent Lithium-Ion Battery State of Charge (SOC) Estimation Methods

By

Shunli Wang, Yujie Wang, Dan Deng,
Carlos Fernandez and Josep M. Guerrero

Cambridge Scholars Publishing

Intelligent Lithium-Ion Battery State of Charge (SOC) Estimation Methods

By Shunli Wang, Yujie Wang, Dan Deng, Carlos Fernandez and Josep M. Guerrero

This book first published 2024

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN (10): 1-5275-5308-6
ISBN (13): 978-1-5275-5308-8

CONTENTS

FOREWORD

To improve the accuracy and stability of power battery state of charge (SOC) estimation, this book proposes a SOC estimation method for power lithium batteries based on the fusion of deep learning and filtering algorithms. This book proposes a SOC estimation method for Li-ion batteries using bi-directional long and short-term memory neural network (BiLSTM), which avoids the problem that the long and short-term memory neural network (LSTM) can only learn in one direction, resulting in poor feature extraction and memory effect in the earlier learning part. For the hyperparameter tuning and time efficiency problems in the training process of the BiLSTM model, the Bayesian optimization algorithm (BO) is introduced for hyperparameter optimization. The training time is shortened, and the optimized model has higher prediction accuracy and stronger generalization ability. Considering the existence of poor stability of this network prediction and the influence of noise, the traceless Kalman filter is used to correct the improved model noise to obtain better tracking accuracy. The authors hope that through their understanding and experience of lithium-ion battery SOC prediction, they can provide some technical references for the design, matching, and application of power lithium-ion battery management systems and contribute to the development of new energy technology applications.

PREFACE

At present, there are many methods to estimate the SOC of a power battery, but there are some limitations. Neural networks overcome the shortcomings of traditional methods, do not need an accurate battery model, and have a strong learning ability. And the estimation accuracy has been improved, which has become a hot research topic in recent years. The change of power battery SOC often shows a certain long-term memory, that is to say, the change rule of SOC is regular in time series. Therefore, starting from the time series of power battery SOC, this book introduces the cyclic neural network model with good time series processing and further excavates the inherent laws of power battery SOC through its unique unit structure. Aiming at the problems of LSTM cyclic neural network in learning time series, such as poor early feature memory and difficulty in fully mining the complete characteristics of the battery, a prediction model of state of charge based on BiLSTM is proposed to improve the accuracy of lithium battery SOC prediction. On this basis, the Bayesian optimization algorithm is introduced to optimize the super parameters in the BiLSTM training process, to improve the estimation accuracy and generalization ability of the LSTM-based power battery SOC estimation model.

Due to the lack of stability of the network model in SOC estimation in the charging and discharging process under different temperatures and working conditions, the unscented Kalman filter algorithm and Bayesian optimized BiLSTM network are designed to fuse, and the improved strategy of the optimized neural network model is explored to form a strong robust algorithm system for SOC estimation. Based on the "one-step prediction, one-step correction" approach, the UKF algorithm uses the mean value of the σ-sampled point set of 2n+1 state quantities in the UT transform in the equivalent circuit model mapping to replace the a priori recursive state of the EKF, which is conducive to reflecting the probability density distribution of state quantities after the nonlinear mapping. At the same time, it avoids the deep learning algorithm to overfit certain outliers and improves the stability and robustness of lithium-ion battery SOC prediction.

CHAPTER 1

INTRODUCTION

1.1. Research background and significance

With the progress of science and technology, the improvement of people's living standards, and the strengthening of environmental awareness, the new energy industry has been developing rapidly. Among them, electric vehicles, as the key to daily travel and material transportation, have become the main driving force for the sustainable and rapid development of the new energy industry. Traditional cars use fossil energy as power, and the huge demand for fossil energy brought by the surge in car ownership exacerbates the pressure of fossil energy production and import in China, which also affects the energy security of China [1, 2]. The process of burning fossil energy in automobiles produces a large number of emissions that are extremely unfriendly to the environment, and these emissions are one of the main causes of haze and PM2.5 [3, 4]. The consumption of fossil energy and the pressure of environmental protection have forced people to seek automotive power sources that can replace fossil energy sources. The development of alternative energy vehicles is a necessary path for the upgrading of China's automobile industry and a strategic measure for the construction of ecological civilization in China [5, 6]. The change curve of China's new energy vehicle production in the past five years is shown in

Figure 1-1.

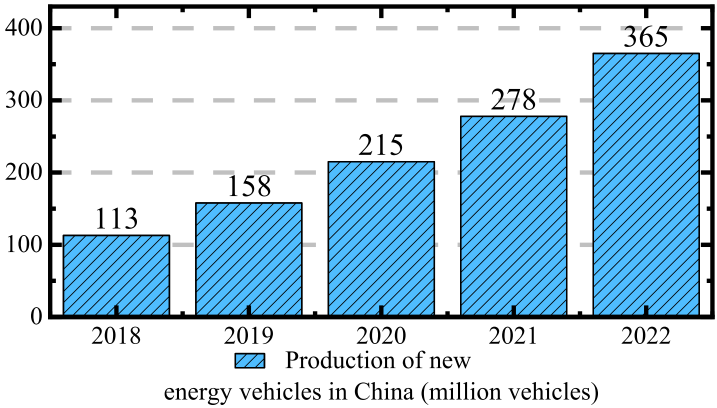

Figure. 1-1 Power lithium-ion batteries shipment trend chart for China

As can be seen from Figure 1-1, under the influence of various factors such as strong support from national policies, continuous breakthroughs in power battery technology, and collaborative development of autonomous driving as well as a more open attitude of consumers, the output of new energy vehicles in China has shown a trend of the year-on-year increase in the past five years. Among them, the lithium battery with its high energy density and long cycle life in the field of new energy vehicles has been developed rapidly [7-9]. According to the Consumer Electronics Association, by 2030, the annual demand for lithium batteries is expected to exceed 2,000 GWh, of which about 85% of the demand comes from the field of electric vehicles, while the remaining part will be used in the fields of aviation power systems [10-12] and energy storage systems [13-16]. For now, the large-scale use of lithium-ion batteries can effectively alleviate the energy scarcity and environmental pollution caused by traditional fossil fuels.

Due to the influence of external environmental factors, especially extreme temperatures, the performance of pure electric vehicles at lower temperatures is much less than that of fuel vehicles [17-20]. The significant inherent differences between the individual cells within the lithium-ion battery pack, as well as its highly nonlinear and multi-coupling nature, make it difficult to improve the accuracy of the intelligent prediction of the state of the lithium-ion battery system, leading to the deterioration of performance, rapid aging, and even spontaneous combustion, and other safety issues are increasingly prominent. To avoid these accidents, the development of a Battery Management System (BMS) has become extremely important [21-23], which can effectively prevent the reduction of battery life due to abnormal conditions such as battery overcharge, over-discharge, and overtemperature.

The State of Charge (SOC) is one of the most central parameters in the whole life cycle of a lithium-ion battery, and its accurate estimation and regulation will affect the output effectiveness and safety of the BMS [24, 25]. Therefore, it is necessary to monitor the changes in this parameter in real-time and guarantee the operating performance of lithium-ion batteries based on this parameter. However, due to the complex and variable load and environmental effects, it is not possible to measure the internal state parameters of the battery directly, and the SOC needs to be estimated indirectly by employing external parameters. Therefore, SOC estimation methods based on external parameters such as voltage, current, and temperature have become a hot research topic.

1.2. Status of domestic and international research on SOC estimation strategies

Battery SOC is a physical quantity that reflects the remaining battery power, and its accurate estimation can effectively reflect the battery efficiency while enhancing the overall performance of the BMS. Conventional SOC is defined as the ratio of the remaining usable battery power to the rated capacity, as shown in Eq. (1-1).

$$SOC = \frac{Q_k}{Q_N} \times 100\% \tag{1-1}$$

In the above equation, Q_k indicates the remaining available capacity of the battery and Q_N is the rated capacity value of the battery.

Specify the lithium-ion battery charge boundary values of 0 and 1, which indicate the battery state when fully charged or the charge is empty, respectively. SOC can also be defined as:

$$SOC = \left(1 - \frac{Q_u}{Q_N}\right) \times 100\% \tag{1-2}$$

In the above equation, Q_u is the capacity of the battery discharging power, and Q_N is the rated capacity value of the battery.

Since the battery SOC is a hidden variable, which leads to the inability to measure directly by sensors to obtain the real data and can only be obtained by indirect methods, it is difficult to calculate the real value of SOC based on the relevant definition of SOC, therefore, the complex and variable SOC estimation method is the key to accurately calculate SOC [26-29].

To dissect the internal and external characteristics of lithium-ion batteries more accurately, it is necessary to establish a high-precision battery system model, design a robust SOC assessment method, and provide a better power battery management system.

1.2.1. Analysis of the advantages and disadvantages of traditional estimation methods

For the exploration of accurate SOC assessment methods for lithium-ion batteries, a lot of research has been conducted in this field in recent years and some results have been achieved. The basic SOC estimation methods include the discharge test method [30-32], the Ampere-hour (Ah) method [33-36], the Open Circuit Voltage (OCV) method [37-40], and so on.

The discharge test method is a discharge experiment on the battery at a constant discharge rate and temperature, and the available capacity of the battery is recorded when the voltage reaches the cut-off condition to achieve an effective estimation of the SOC value of lithium-ion batteries. The method is simple in operation and applicable to different types of power batteries, but the measurement period is long and the SOC value can be obtained only when the complete discharge to the cut-off voltage must be satisfied, which is mostly used for pure off-line measurement in the laboratory. Therefore, it is difficult to estimate the SOC value of the battery in the actual working condition.

The computational idea of the ampere-hour integration method is to achieve SOC estimation by accumulating the incoming and outgoing power when the lithium-ion battery is charged and discharged, which can be measured online [41]. Ding et al. [42] used the Ah method with the Unscented Kalman Filter (UKF) algorithm to compensate for the fitting error generated by the model identification process of battery SOC in the 0.9-1 interval in SOC estimation under complex operating conditions, and the estimation accuracy is high. However, this method is overly dependent on the initial value of SOC, ignoring the influence of multiple external factors, and there is a serious cumulative error along with the extension of the operation cycle.

The open-circuit voltage method is to sit the battery for a long enough time, and after the internal state of the battery is stabilized, the battery SOC is deduced from the mapping relationship between OCV and SOC. Sun et al. [43] used the available capacity at different temperatures to construct the battery OCV-SOC function relationship to achieve an effective estimation of SOC. Chen et al. used constant current discharge experimental data to develop a synergistic prediction of OCV and internal resistance of lithium-ion batteries to achieve accurate SOC estimation. The method is simple and convenient, and the SOC can be achieved directly from the measured value OCV. However, the shelving time is long and it is difficult to perform online measurements during vehicle start-up.

1.2.2. Exploration of Nonlinear Observers Based on Models

The model-based estimation method transmits the experimental battery voltage, current, and temperature as input signals to the battery model, to perform accurate online identification of the battery model parameters, and finally to fuse them with a nonlinear observer to achieve accurate dynamic estimation of the battery SOC. The most commonly used nonlinear observer is the Kalman Filter (KF) algorithm [44-49]. The core idea of KF is to use the battery current moment measurement data to make a one-step prediction of the previous moment and filter out some noise disturbances through iterative operations to obtain the optimal estimate of the system state at the next moment. The structure of the estimation method is shown in Figure 1-2.

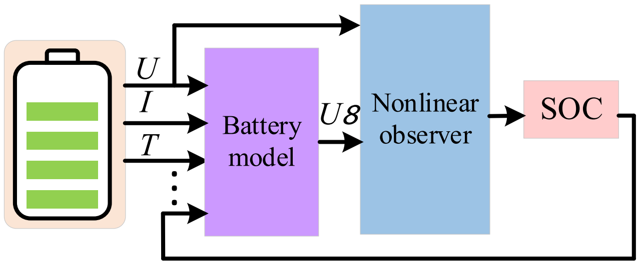

Figure. 1-2 Structure of the model-based SOC estimation method for lithium-ion batteries

To accurately simulate the response characteristics under different operating conditions, the equivalent circuit model [50-55] is chosen as the mathematical model. Equivalent circuit models are widely used in the electrical field because of their intuitive mathematical expressions, powerful dynamic characterization capability, and high accuracy [56-59]. Based on the equivalent model, it is especially important to identify the model parameters accurately. He et al. [60] explored a variable parameter equivalent hysteresis model based on the Thevenin model. The model fully considered the effects of temperature and SOC variations on model accuracy but ignored the effects of electrochemical reactions within the Thevenin model. Wang et al. [61] constructed a spliced equivalent circuit model (S-ECM) and obtained accurate mathematical expressions under complex operating conditions. However, the model requires the identification of too many parameters, which increases the computational complexity. Yang Xiao et al. [62] explored a restricted memory forgetting factor recursive least squares (LM-RLS) method to identify model parameters online while using the extended Kalman filter (EKF) algorithm to estimate the SOC to achieve high accuracy evaluation of the SOC of Li-ion batteries. Zheng et al. [63] proposed a bias-compensated recursive least squares (BCRLS) method to identify model parameters. However, this algorithm strongly relies on the a priori estimation of the noise covariance.

The KF algorithm belongs to the recursive algorithm, which is usually used in dynamic systems with unknown initial values to effectively correct the system state variables, is strongly adaptive for strongly nonlinear systems, and can evaluate the effect of SOC estimation for operating electric vehicle lithium-ion batteries in real-time [57, 64-69]. Jiang et al. [70] proposed a new adaptive square root extended Kalman (ASR-EKF) filter that can solve the filter divergence problem caused by computer rounding errors, but ignores the unknown and uncertainty of the system noise. Chen Zonghai et al. [71] used particle filtering for online estimation of open-circuit voltage to achieve voltage-based battery state estimation. Du et al. [72] proposed an adaptive fading traceless Kalman filter (AFUKF) method to solve the extreme inconsistency problem of retired batteries and improve the adaptability and robustness of process modeling errors. However, the method does not address the nonnegativity characteristics of the matrix and does not adequately consider the estimation performance at different time scales. Shen et al. [73] developed a square root cube Kalman filter (SRCKF) method to estimate the battery SOC. The method avoids the filter divergence problem under strongly nonlinear operating conditions and has strong robustness and convergence. However, it is difficult to balance the state estimation error caused by the ratio of a priori estimates and posterior feedback measurements. Based on the reverse recursion of past data, Ding Jie proposed a weighted $H\infty$ filtering algorithm that can update the algorithm SOC value online with a stable error within 3% and a convergence speed better than that of the sliding mode observer. The strong correction capability of the filtering algorithm [46, 74-79] makes this type of estimation method the mainstream direction of SOC estimation [80-84], but it has a strong dependence on the accuracy of the model and is computationally complex and redundant, and takes a relatively long time.

In recent years, with the rise of concepts such as artificial intelligence and big data, more and more machine learning methods have been tried in the SOC estimation of electric vehicle-powered lithium-ion batteries, and emerging algorithms based on data mining have made certain achievements.

1.2.3. Research on data-driven self-learning mechanisms

The data-driven approach is a direct estimation of SOC from a large number of data samples of battery measurement parameters such as current, voltage, temperature, etc. through a "black box". This black box does not need to consider the internal characteristics of the battery does not rely on an accurate model, and has good nonlinear mapping capability [85-87]. The data-driven estimation method is shown in Figure 1-3.

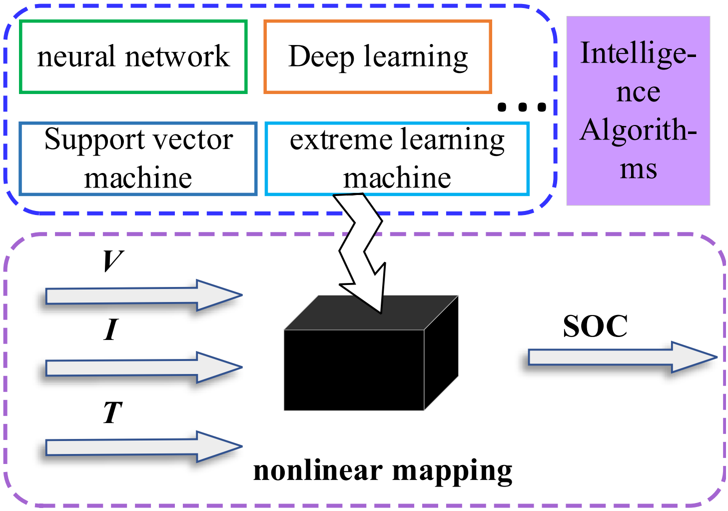

Figure. 1-3 A data-driven approach to SOC estimation

Common data-driven SOC estimation methods based on support vector machines (SVM) [88-91] and extreme learning machines (ELM) [92-98] and neural networks (NN) [99-104] are available.

The theoretical basis of the SVM method is nonlinear mapping, which has strong performance advantages for nonlinear systems as well as high-dimensional spaces. However, the method is difficult to implement for large-scale training samples and is only applicable to small-sample data training. Yang [105] proposed the least squares support vector machine (LS-SVM) for estimating the SOC values of lithium-ion batteries. The method was tuned for model complexity and generalization to overcome the training overfitting problem.

The ELM algorithm does not require iteration of the hidden layer for model training and learning, and it has the advantages of fast convergence and high generalizability, but it can only be used to explore lightweight samples to prevent the overfitting phenomenon, which is less controllable. Liu et al. [106] proposed a SOC estimation method based on ELM and maximum correlation entropy square root volume Kalman filter (MCE-SRCVKF) to reduce the impact of noise on SOC estimation accuracy, which reduces the impact of measurement noise while simplifying the tuning process and has strong robustness.

Neural networks are widely used for their good self-learning capability to effectively deal with strong nonlinearities and can accurately track the actual SOC values when there is a large amount of sample data without the need to build a specific model and consider the internal operating characteristics of the battery [100, 107-109]. Ma [110] performed a collaborative estimation of SOC and state of energy (SOE) of lithium batteries based on a long short-term memory (LSTM) neural network in a complex operating environment. The average absolute errors of SOC and SOE estimation were only 0.91% and 1.09%, which verified the high accuracy and strong robustness of the method. Hu [111] constructed an online SOC estimation model based on a radial basis neural network (RBFNN) to solve the battery nonlinearity problem. However, it cannot adapt to complex and variable driving conditions and is prone to large error deviations of SOC estimation results under complex operating conditions. Chunsong Lin et al. [22] used a differential evolutionary algorithm to optimize the neural network to obtain the global optimal solution, and the estimation accuracy of power battery SOC was improved. The neural network-based SOC estimation method can improve the SOC estimation accuracy, but the large sample data required will lead to a long training time for the model, which leads to the overlearning phenomenon.

1.2.4. Study of estimation strategies based on hybrid algorithms

For SOC estimation of lithium-ion batteries, there are numerous methods and their respective superiority, but they also possess certain limitations. To further improve the accuracy of SOC estimation for lithium-ion batteries and to compensate for the shortcomings of a single estimation method itself, researchers have proposed hybrid algorithmic strategies, such as the interfusion of data-driven models [112-116]. Chen et al. [117] proposed a SOC estimation method that fuses LSTM neural networks and adaptive H∞ filters, which reduces the output fluctuations of LSTM networks and omits the traditional observer's exact modeling task. Proenza-Perez et al. [118] designed a hybrid algorithm integrating the UKF algorithm with the BP (backpropagation) neural network for estimating battery SOC estimation, which corrects the estimation error of UKF and further improves the estimation accuracy of the BP network. Chen [119] used the robust recursive least squares (RRLS) method to extract the equivalent circuit model online parameters and incorporate them into the HIF algorithm to achieve accurate estimation of SOC, this hybrid method incorporates parameter estimation error in the discriminative model, which can effectively reduce the unknown noise interference caused by model error. Yang et al. [120] used a combination of LSTM and UKF to estimate the SOC of lithium-ion batteries, which enhanced the stability of the network model and filtered the noise interference but did not consider the ambient temperature and the battery aging condition effects.

With the rapid development of intelligent algorithms, data mining methods combined with model-based filtering algorithms are widely used and have achieved significant results. For a priori estimation, the model-based filtering algorithm plays a decisive role in estimation, while for the case of an unknown model, the data-driven method can estimate SOC performance more accurately. In this book, we aim to build a dynamic model with data-driven and Kalman filtering, optimize and improve the neural network model, and then introduce the improved Kalman filtering algorithm to estimate and correct the network model noise, which effectively solves the problems of low accuracy, poor robustness and slow convergence of SOC estimation.

1.3. Research content and structure of the project

1.3.1. Research content

As a technical bottleneck for the promotion and development of electric vehicles, the accurate state prediction of power lithium-ion batteries is important to strengthen the real-time monitoring function of BMS and ensure the safe and reliable operation of power lithium-ion batteries. In this book, we analyze the coupling relationship between the key operating characteristics and SOC of power lithium-ion battery, obtain the model input data under complex operating conditions, and establish a dynamic SOC prediction model based on Bidirectional Long Short-Term Memory (BiLSTM). To address the problem of the tedious and difficult selection of model hyperparameters, Bayesian Optimization (BO) is used to optimize the model hyperparameters and obtain high-accuracy prediction results. The optimization model improvement strategy is explored, and the UKF algorithm is used to correct the model noise interference to form a strongly robust charge state estimation algorithm system, as shown in Figures 1-4.

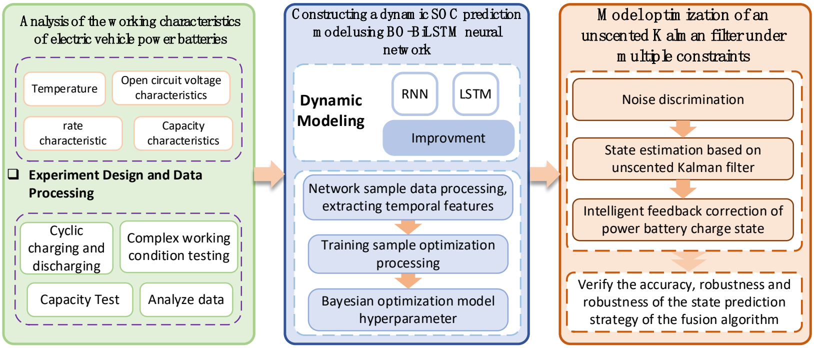

Figure. 1-3 Research content

1.3.2. Organization structure

According to the general description of the study, the specific structure of this book is arranged as follows:

Chapter 1: Introductory section. The development of electric vehicles and their lithium-ion batteries and their future dynamics are discussed, the definition of SOC is clarified, the scientific achievements of lithium-ion batteries at home and abroad at this stage are summarized, and their advantages and disadvantages are analyzed, and the research direction of this book is finally clarified.

Chapter 2: Analysis of the working characteristics of power lithium-ion batteries. The internal structure and electrochemical reactions of lithium-ion batteries are explored, and the mapping relationship between battery operating characteristics and key parameters is further investigated. The internal and external characteristics analysis is carried out with full consideration of the input and output characteristics under complex operating conditions, and the influence of different temperatures on the internal parameters of the powerful lithium-ion battery is explored to obtain the evolution law of the key parameters and performance of the lithium-ion battery.

Chapter 3: Bayesian optimization of the BiLSTM battery SOC dynamic prediction model. Firstly, the LSTM-based SOC prediction model is constructed, and the inverse sequence is added to form the BiLSTM dynamic model considering the problems of difficult training and poor generalization performance of future timing characteristics. The BiLSTM model hyperparameters are configured using a Bayesian optimization algorithm to seek the best hyperparameter combination to improve the model training capability and optimize the performance characteristics.

Chapter 4: Exploration of noise correction strategy by fusing Kalman filter. A battery equivalent model is constructed and a rectangular window recursive least square (RW-RLS) is proposed for online identification of the relevant parameters of the equivalent model to obtain a high-precision modeling system. For the interference of system time-varying noise, the UKF algorithm is chosen to avoid the filtering divergence, while the noise is corrected based on the Sage-Husa algorithm. The design fusion optimization strategy achieves strong robustness and adaptive state estimation.

Chapter 5: Verification of state estimation algorithm under simulated working conditions environment. The experimental test platform is constructed and designed to obtain the battery input characteristics under complex simulated operating conditions. Suitable performance indicators are selected to analyze and compare the prediction effects of the involved models for validation.

Chapter 6: Summary and Outlook. The main work of this book is summarized, the shortcomings of the proposed method in the research process are analyzed, and the outlook on the subsequent research directions is made.

CHAPTER 2

ANALYSIS OF THE OPERATING CHARACTERISTICS OF POWER LITHIUM BATTERIES

From the analysis of the research background in Chapter 1, it can be seen that new energy vehicles are developing rapidly, and lithium-ion batteries have become the preferred power source for new energy vehicles due to their performance advantages. Deep exploration of battery technology is crucial in the field of new energy. This chapter will provide an in-depth analysis of the working mechanism and characteristics of lithium batteries, laying the foundation for extracting input characteristics of SOC estimation models for power lithium-ion batteries and constructing high-precision equivalent models.

2.1. Research on the Internal Working Mechanism of Power Lithium Batteries

As a portable energy storage element, the lithium-ion battery has the advantages of high combustion value, environmental protection, long cycle life, no memory effect (capacity loss), good safety performance, low self-discharge, fast charging, wide operating temperature range, etc. Lithium ions generally include the main structures of the positive electrode plate, negative electrode plate, electrolyte, and separator. The positive electrode plate provides Li^+ for the battery, while the negative electrode plate is mainly graphite. The diaphragm is a special type of microporous film that can prevent the unrestricted transfer of electrons between the positive and negative electrodes of the battery, allowing only Li+ to travel back and forth [121-125]. Lithium ions generate electrical energy by constantly moving back and forth between the positive and negative electrode plates and can charge and discharge repeatedly. The internal structure of lithium ions is shown in Figure 2-1.

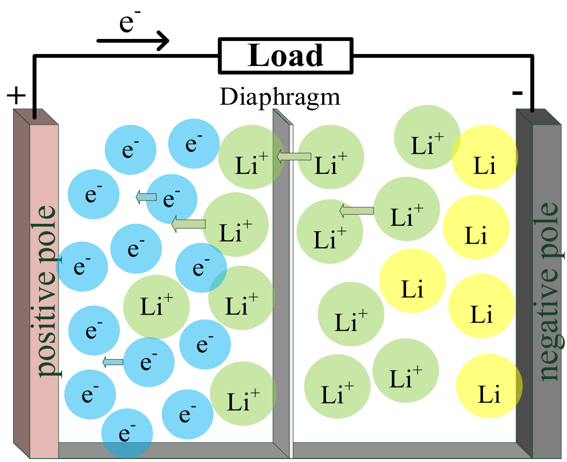

Figure 2-1 Schematic diagram of the structure of a lithium-ion battery

From Figure 2-1, it can be observed that during the charging action of the battery, the positive electrode material undergoes an oxidation reaction, releasing electrons. The positively charged Li+ passes through the electrolyte solution and the separator to reach the carbon layer of the battery's negative electrode, and the negative electrode obtains Li+. During the discharge action, Li+ detaches from the negative electrode and integrates into the positive electrode through the corresponding electrolyte and membrane micropores, achieving mutual conversion between electrical and chemical energy [126-129]. The internal chemical reaction process of lithium-ion batteries is described in Figure 2-2.

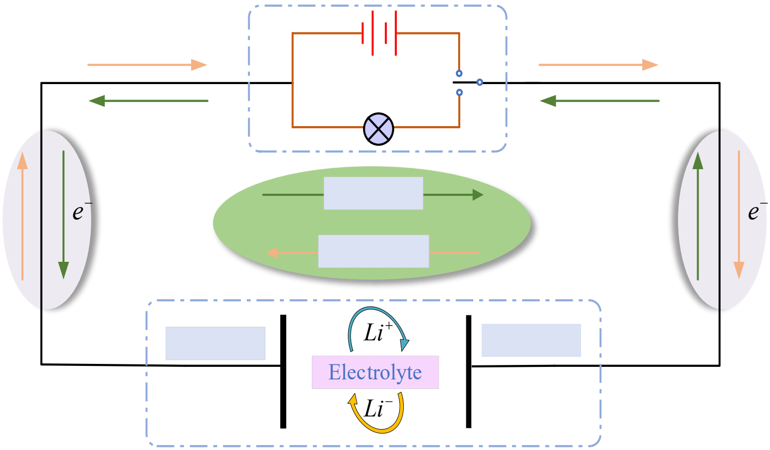

Figure. 2-2 Internal chemical reaction process of lithium-ion battery

The chemical transformation equations for the positive and negative reactions of lithium-ion batteries and the total reaction of the battery can be described as formula (2-1).

$$\begin{cases} P: LiM_xO_y = Li_{(1-x)}M_xO_y + xLi^+ + xe^- \\ N: nC + xLi^+ + xe^- = Li_xC_n \\ T: LiM_xO_y + nC = Li_{(1-x)}M_xO_y + Li_xC_n \end{cases} \tag{2-1}$$

As a high energy density battery with excellent development prospects, lithium-ion batteries can achieve the extraction of multiple Li+ between plates. As the internal structure changes, the internal performance of the battery will also decrease. Therefore, exploring the internal mechanism of batteries is beneficial for assisting in exploring the working characteristics and performance evolution of batteries.

2.2. Analysis of Key Parameter Characteristics of Power Lithium Battery

2.2.1. Analysis of open-circuit voltage Characteristics

The open circuit voltage of a battery refers to the terminal voltage between the positive and negative poles when there is no load on the external circuit of the battery. After the battery has been left standing for a sufficient time, the internal electrochemical reaction gradually stabilizes, and the default OCV of the battery is approximately equal to the current electromotive force. Research has shown that there is a relatively stable functional relationship between the open circuit voltage OCV and SOC when charging and discharging the battery in a constant temperature environment of 25 °C. Based on this relationship, effective characterization of battery OCV-SOC was obtained using function fitting tools to more intuitively reflect the static SOC characteristics of the battery [43, 130-134]. The experimental OCV-SOC relationship of the battery is shown in Figure 2-3.

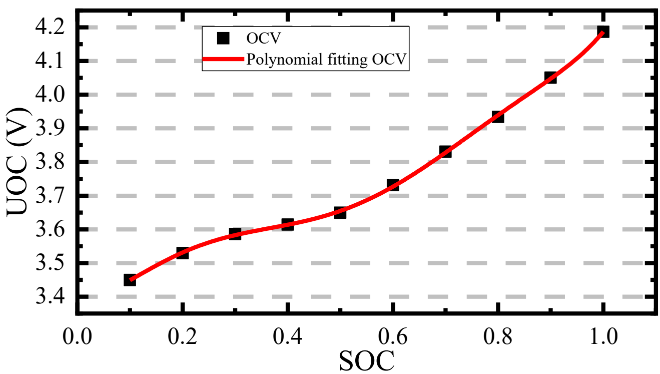

Figure. 2-3 Graph of OCV-SOC curve at 25°C