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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**ONLINE ESTIMATION OF KEY BATTERY STATES FOR
MANAGEMENT OF VANADIUM REDOX FLOW
BATTERY**

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2017

ONLINE ESTIMATION OF KEY BATTERY STATES FOR MANAGEMENT OF VANADIUM REDOX FLOW BATTERY

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Summary

Rechargeable battery systems are experiencing rapid advancement due to their pivotal roles in the renewables penetration, smart grid formation and transport electrification. Among various rechargeable battery systems, the all-vanadium redox flow battery (VRB) has received extensive attention especially in the field of large-scale energy storage. To enhance the reliability, efficiency, and longevity, the battery management system (BMS) has to be well-designed to supervise the operation of VRB. In this thesis, focuses are given to the investigation of online battery model identification and the associated estimation methods to keep track of the essential battery states including the peak power, the state of charge (SOC), and the instantaneous capacity.

Reliable state estimation depends directly on an accurate battery model. However, the parameters of battery model are time varying with the operating condition variation and battery aging thus the common methods where model parameters are prescribed offline are not adequate. To address this issue, the first part of this thesis proposes to use an online adaptive battery model to reproduce the battery dynamics accurately. Two algorithms including the recursive least squares (RLS) and the extended Kalman filter (EKF) are compared on the ability of online model parameters identification and the RLS proves to be superior considering the modeling accuracy, convergence, and computational complexity. The peak power is an essential state defined as the maximum power that is possible to be accepted or delivered by the battery at a specific operating point without violating the Safe Operating Area (SOA). Based on the online identified battery model, an adaptive peak power estimator which incorporates the constraints of voltage limit, SOC limit and design current limit is proposed to fully exploit the potential of VRB. The proposed peak power estimator is verified with a “two-step verification” method. The influence of prediction time horizon on the peak power is also analyzed.

The abovementioned model identification method relies on an open-circuit cell to accurately measure the open circuit voltage (OCV). Using such an additional cell, however, will increase the configuration complexity of the VRB system. To tackle

this problem, a new online model identification method without requiring the open-circuit cell is proposed and based on which an online SOC estimation method is investigated in the second part of the thesis. Two main contributions have been drawn. Firstly, the estimations of model parameters and OCV are fully decoupled to rule out the possibility of cross interference between them. Secondly, multiple timescales are adopted for different estimators by analyzing the model sensitivity, stability, and accuracy. Based on the proposed multi-timescale estimator, the SOC is inferred directly from the SOC-OCV look-up table. Experimental results show that the proposed method is highly accurate and also robust to the initialization uncertainty and operating condition variation. The robustness to battery aging is also satisfactory within an aging degree of 14.78%.

As another crucial index, the instantaneous capacity is a figure of merit describing the state of health (SOH) of the battery. The accurate update of capacity also contributes to improving the accuracy of the SOC estimate. Driven by this, the third part of the thesis focuses on the adaptive joint estimation of SOC and instantaneous capacity based on an online identified battery model. The model parameters are online adapted with the RLS method, based on which an EKF-based novel joint estimator is formulated to estimate the SOC and capacity concurrently. The proposed joint estimator compresses the filter order effectively which leads to a substantial improvement in the computational efficiency and numerical stability. Lab scale experiments are carried to show the fidelity of the proposed method. The comparison with other existing methods also suggests its superiority in terms of accuracy, convergence speed, and computational cost.

The existence of noises is unavoidable in real applications and may decline the accuracy of both the model identification and state estimation. In the last part of this thesis, therefore, the effect of measurement noises is investigated. It is shown that the common methods for model identification are intrinsically biased if both the current and voltage sensors are corrupted with noises. The uncertainties in the battery model further degrade the accuracy of the SOC estimate. To address this problem, a novel technique which integrates the Frisch scheme based bias compensating recursive least squares (FBCRLS) with a SOC observer is proposed

to enhance the model identification and SOC estimate. The proposed method estimates the noise statistics and compensates the noise effect so that the model parameters can be extracted without bias. The SOC is further estimated in real time with the online updated and unbiased battery model. Both simulation and experimental studies are carried out to show the validity of the proposed method.

The thesis provides a set of data-driven based algorithms for the reliable and high-fidelity online estimation of key battery states. As only the onboard measured current and voltage signals are required, the proposed algorithms are also promising to be generalized to a broad range of other battery chemistries.

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List of Symbols

s	SOC
η	coulombic efficiency
I_L	load current
Q	capacity
k	time index
V_t	terminal voltage
R_s	ohmic resistance
R_p	polarization resistance
C_p	polarization capacitance
V_{oc}	OCV
V_p	polarization voltage
M	hysteresis level
ζ	user-defined threshold
h	hysteresis voltage
H	the maximum hysteresis voltage
w	process noise
v	measurement noise
Σ_w	covariance matrix of process noise
Σ_v	covariance matrix of measurement noise
Σ_x	state covariance
$V_{t,min}$	lower cut-off voltage
$V_{t,max}$	upper cut-off voltage
L	prediction time horizon for peak power
$I_{L,max}^{dis,volt}$	peak discharge current under voltage constraint
$I_{L,min}^{chg,volt}$	peak charge current under voltage constraint
s_{min}	lower bound of SOC
s_{max}	upper bound of SOC

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$I_{L,\max}^{dis,soc}$	peak discharge current under SOC constraint
$I_{L,\min}^{chg,soc}$	peak charge current under SOC constraint
$I_{L,\max}$	design limits of discharge current
$I_{L,\min}$	design limits of charge current
$I_{L,\max}^{dis}$	peak discharge current under multiple constraints
$I_{L,\min}^{chg}$	peak charge current under multiple constraints
P_{dis}	discharge power sequence under peak current for the prediction time horizon
P_{chg}	charge power sequence under peak current for the prediction time horizon
P_{peak}^{dis}	peak discharge power
P_{peak}^{chg}	peak charge power
Δt_I	timescale of OCV estimator
n	sampling interval used to update the OCV
u	model input
y	model output
ϕ	parameter vector
ε_1	error term of the OCV estimation
$\Lambda \varepsilon_I$	additional error term caused by the identification errors
ΛR_s	identification errors on R_s
ΛR_p	identification errors on R_p
ΛC_p	identification errors on C_p
ΛV_{oc}	variation of OCV estimation caused by the additional error
ΔV_t	differential voltage
ΔI_L	differential current
Δt_2	timescale of R_s estimator
ε_2	error term of the R_s estimator
Δt_3	timescale of R_p and C_p estimation
ε_3	error term for the R_p and C_p estimation
Φ	disturbance

LIST OF SYMBOLS

z	discretization operator
n_p	order of polynomial fitting
Δt_c	time interval used to identify the model parameters
$e_1(t)$	error term of the model parameter estimator
$e_2(t)$	error term of the simple OCV estimator
λ	forgetting factor
x	state vector
L	feedback gain
θ	parameter vector to be estimated
φ	input vector
σ_i	variance of current noise
σ_v	variance of voltage noise
$\tilde{I}_L$	measurement noise on I_L
$\tilde{V}_t$	measurement noise on V_t
Γ_p	auto covariance matrix of arbitrary vector p
Γ_{pq}	cross covariance matrix of two arbitrary vectors p and q
χ_{pr}	cross covariance matrix between arbitrary vector p and a stochastic process r
$E(\bullet)$	expected value operator
$\mathcal{G}$	vector argument
δ_0	instrument vector
Cf	cost function
μ	step-size parameter
$\Re(\bullet, \bullet)$	Rayleigh quotient
$r(\bullet)$	remainder term of Taylor approximation

List of Acronyms

RFB	redox flow battery
VRB	all-vanadium redox flow battery
OCV	open circuit voltage
SHE	standard hydrogen electrode
BMS	battery management system
SOC	state of charge
SOH	state of health
SOF	state of function
ECM	equivalent circuit model
PDE	Partial differential equation
ANN	artificial neural network
SVM	support vector machine
RBFNN	radial basis function neural network
SFNN	square of correlation coefficient
LSSVM	least square support vector machine
ESC	enhanced self-correcting
DP	dual polarization
EKF	extended Kalman filter
CC	coulomb counting
EMF	electromotive force
AC	alternating current
DC	direct current
KF	Kalman filter
SPKF	sigma-point Kalman filter
UKF	unscented Kalman filter
CDKF	central difference Kalman filter
AEKF	adaptive extended Kalman filter
AUKF	adaptive unscented Kalman filter
PF	particle filter

LIST OF ACRONYMS

UPF	unscented particle filter
SMO	sliding mode observer
NPF	nonlinear predictive filter
DEKF	dual extended Kalman filter
JEKF	joint extended Kalman filter
LS	least squares
RLS	recursive least squares
ELM	extreme learning machine
DNPF	dual nonlinear predictive filter
DSPEK	dual sigma-point Kalman filter
SOA	Safe Operating Area
PNGV	Partnership for New Generation Vehicles
HPPC	hybrid pulse power characterization
EP	electrochemical-polarization
SOP	state of power
RELS	recursive extended least squares
CPE	constant phase element
LTV	Linear time varying
CCCV	constant current- constant voltage
BCRLS	bias compensating recursive least squares
EIV	error-in-variables
FBCRLS	Frisch scheme based bias compensating recursive least squares
BCLS	bias compensating least squares
EVD	eigenvalue decomposition
RQ	Rayleigh quotient
YW	Yule-Walker
MSD	mean square deviation
MAE	mean absolute error
MRE	mean relative error
RMSE	root mean square error

CHAPTER 1 Introduction

1.1 Background

1.1.1 Renewable Energy and Electrical Energy Storage

Energy is the lifeblood of modern society. The emerging concerns over the fossil-fuel supplies depletion, global warming and environmental pollution have led to increasing interests in the utility of renewable energies. It is a common sense that the oil reserves will be exhausted in a few decades and 2057 has been estimated to be the year when oil depletion happens [1]. Twenty-nine states in the United States have issued the renewable portfolio standards that mandate 15–30% renewable electricity sales by 2025 [2].

Due to the high demand of green energy utilizing, the solar and winding power generations as the primary sources of renewable electricity production for the grid have been brought to the forefront. These renewable energy sources, unfortunately, are highly intermittent and difficult to control, thus reliable electrical energy storage (EES) systems are highly required for stable and consistent power delivery in the integration of renewable energy into the grid. Currently the power capacity for EES within the grid is about 125 GW which is only about 3% of global power capacity and the majority of EES is in the form of pumped hydroelectric storage (PHS). Considering this, additional EES systems are expected to be integrated within the grid and this will allow more plants to run closer to full capacity. EES has been playing a key role in diversifying the energy sources and adding more renewable energy sources into the existing energy market. Take the large stationary EES of power grid for example, the benefits of EES include peak power shaving, load levelling, and standby reserve [3]. On the other hand, the penetration of battery-powered EVs into the market is quite urgent to reduce the CO₂ emission and to alleviate the heavy dependence on fossil fuels, considering the growing number of transportation vehicles and the associated negative consequences. EES has thus emerged as a top concern for the future smart grid and EVs.

EES technologies have been developed to face the aforementioned challenges for years. To date, the state-of-the-art EES technologies include PHS, thermal energy storage (TES), superconducting magnetic energy storage system (SMES), compressed air energy storage system (CAES), recharging battery, flywheel, and super-capacitor. Among multiple types of EES systems, rechargeable batteries are the most promising to meet the future needs because of their high energy efficiency [4]. Battery storage has been viewed as the essential technique for the renewables penetration, transportation electrification, and smart grid establishment. Driven by the urgent demand, battery technology has been growing rapidly towards high performance and low cost.

1.1.2 Research Interests on Vanadium Redox Flow Battery

Among different flavors of battery chemistries, the VRB proposed by Skyllas-Kazacos [5, 6] and co-workers has shown great potential due to the unique merits including elimination of cross contamination, independent capacity and output power design, tolerance to deep discharge, high energy efficiency and long life cycle [7, 8]. Therefore, the VRB technique is viewed as a promising solution to the energy storage market.

Although the concept has been proposed many years ago, the VRB is still in its infancy stage with respect to the commercialization and developmental maturity, with almost all the related techniques under development from the perspective of real applications. To date, most of the efforts have been given to the field of design, manufacturing, and use of various separator/membrane materials, as all these are critical and have large impacts on the power performance and lifetime of VRB. Electrolyte mixtures containing various additives with different concentrations have been shown to facilitate improving the energy density, increasing the range of working temperature, and reducing the cost of production. A majority of efforts from the researchers have been made to explore the high-quality membrane materials with high ionic conductivity and good resistance to the battery degradation. The researches on electrode material, design, and manufacturing have been focused on reducing the reaction inefficiencies through increasing the

conductivity and surface area of the electrodes [9].

While there have been intensive investigations on the cell design, testing, and performance enhancement, the issues in real applications have not been addressed adequately. Even the fundamental operational methods such as SOC estimation, SOH monitoring, power prediction, flow rate control, and charge discharge characteristics are still under development. Although lots of models have been investigated, they are mostly the complicated electro-chemical model, electro-thermal model, and multi-physics model which are computationally expensive and are aimed majorly for design optimization. The VRB models with low complexity that enables the electronics interfacing and supports the system-level supplication are still under development.

1.1.3 Battery Management System

While the battery technologies are advancing very quickly on developing cells with higher power and energy densities, it is equally important to improve the performance of the BMS to enhance the safety, reliability, and cost efficiency of the battery system. The BMS should be equipped with accurate algorithms to monitor and estimate the functional status of the battery and meanwhile the state-of-the-art mechanisms to protect the battery from the low operating efficiencies and even the potential hazardous. The basic responsibilities of the BMS are summarized as:

(1) Battery parameters detection

This includes the basic current detection, voltage detection, temperature detection, insulation detection, impedance detection and so on.

(2) Safe operations

This includes thermal management, operating between safe current and voltage limits, shutdown on detection of fault, etc. The thermal management system is critical important for the VRB operation. It has been shown that the electrolytes of VRB should be strictly controlled within a specific temperature range for the battery to work efficiently [10]. For typical VRB electrolytes with 1.8 - 2 M vanadium

sulphate in 2.5 - 3 M sulfuric acid, the thermal precipitation of V^{5+} will happen when the temperature is higher than 40°C over extended periods, while the precipitation of V^{2+}/V^{3+} will occur when the electrolyte temperature drops below 5°C [11]. The overall efficiency of VRB will drop significantly if the VRB system works outside the recommended temperature range. A more severe consequence of lacking thermal management is that the precipitation can block the electrolyte channels and leads to safety hazards. Although the precipitation can be minimized by reducing the vanadium ion concentration below 1.8 M, this inevitably leads to a reduced energy density which is undesirable in the real applications. For this purpose, a reliable thermal management system is the prerequisite of the high-efficiency operation of the VRB.

(3) Online state estimation

This includes the SOC or depth of discharge (DOD), SOH, peak power, and remaining useful life (RUL), etc. The SOC or DOD of batteries is estimated by measuring working current, temperature, and voltage. For the closed-cell systems, the SOC determination will be quite challenging as it cannot be measured by any available sensors. The VRB allows using an open-circuit cell to measure the OCV and then inferring the SOC, but the additional sensors and the installation of open-circuit cells can add complexity to the already complicated system. SOH is estimated according to the extent of abuse and performance degradation of batteries. Peak power is essential for the power management by judging the maximum input or output potential of battery for the next operating time horizon.

(4) On-board diagnosis

The typical faults include sensor fault, network fault, battery fault, over-charge, over-discharge, overcurrent, abnormal temperature, loose connection, insulation fault, and so on [12].

(5) Charge control

On the basis of the battery limitation and the power limitation of charger, BMS should decide the optimal charging strategy to make trade-off between charging

speed, charging efficiency, temperature rise and battery degradation.

(6) Cell balancing

For lithium-ion batteries and other closed-cell systems, the BMS should also be able to handle an additional function of cell balancing. Cell-to-cell variations are one of the reasons for the degradation of the battery pack. In order to avoid premature cell degradation and minimize the safety hazards, the upper limit and lower limit voltage of a single cell block must not be exceeded. Therefore, the actual capacity of the pack is constrained by the cell block that firstly reaches the voltage limits. In this regard, the remaining capacity of the other cell blocks will be wasted. Fortunately, the VRB system can avoid the above mentioned imbalance. This is because the electrolytes from the same external reservoirs are circulated through all the battery stacks. In this way, all the system components share the active species with the same properties thus the imbalance can be minimized. Considering that the balancing system especially for the non-dissipative balancing systems are usually very complex, including both power electronics and control networks, it is a very expensive component in BMS. In this regard, the feature of VRB actually helps to save lots of costs by omitting the balancing system.

Other issues related to the BMS may include the electrolyte flow rate control in accordance with the power demand; which is only applicable for flow battery, and other miscellaneous functions.

1.1.4 Online Estimation of Key Battery States

The SOC is the most important state in BMS and any other management issues require the accurate estimation of SOC as prerequisite. The SOC, which is used to describe its remaining capacity, reflects the battery status to determine how long the cell will last and is the indicator on when to stop charging and discharging. Therefore, the accurate estimation of SOC can not only protect battery from the rapid aging or damage caused by the unsuitable over-charge and over-discharge, and improve the battery life, but also allow the application to make rational control strategies to save energy.

Although the VRB systems have low possibility of ignition and explosion, the unsuitable over-charge and over-discharge can still degrade the battery significantly. While no morphological changes limit the depth of discharge, the over-discharge can lead to the cell reversal, which is definitely undesired. Gassing side reactions will occur at both half-cells and cause fading of capacity [13]. The hydrogen evolution at the negative half-cell is significant above 90% SOC. Severe over-charge conditions can also deteriorate the electrode materials. Therefore, the accurate estimation of SOC is critical to improve cell performance and to extend the service life. In real applications, the BMS regulates the battery to work within a specific SOC range. In this regard, the accurate estimation of SOC contributes to fully exploiting the remaining energy in the battery. Assume the theoretical SOC range is from 10% to 90%, the possible operating range of battery is only 20% – 80% if a 10% error on SOC estimation exists. This means a waste of 20% on the battery capacity. In order to fulfill the capacity requirement for specific applications, an additional design capacity of 20% actually represents a great increase of cost. To this end, the accurate estimation of SOC is also of great importance from the cost perspective. In summary, the online SOC estimation methods with high accuracy and robustness is essential regardless the field of use.

It is known that the battery system will degrade during cycling even under normal operation. This degradation can be accelerated by extreme load patterns, abnormal temperature, over-charging, or over-discharging. The degradation will result in the increase of internal resistance and more importantly the fade of battery capacity. It is a basic function of BMS to know the health state of the battery in use and the remaining service life of battery. SOH is the indicator to reflect the battery's life and health status by indicating the ability of the battery to perform well both in charge and discharge. Through the accurate estimation of SOH, it may be possible to know the aging or degradation of the battery and whether the battery should be replaced or not. The parameters to evaluate the SOH include the internal resistance and the actual capacity, while capacity is more straightforward and can be viewed as the primary indicator. Generally, if the battery capacity fades by 20% of the initial value, indicating the SOH drops to 80%, the BMS would warn the user to change the batteries [14]. Knowing SOC and SOH further provides the estimate of state-of-

function (SOF).

The peak power is an essential state defined as the maximum power that is possible to be accepted or delivered by the battery for the future prediction time horizon without violating the safety requirements. The reliable estimate of peak power enables the system to fully exploit the potential of battery within the safe operation window. Taking the VRB/photovoltaic-based microgrid system demonstrated in ref. [15] as an example, if the VRB cannot deliver enough discharging power at night when the power from the PV array drops to zero, the user-end requirement cannot be fulfilled. Alternatively, if the remained PV power is beyond the acceptable range of VRB, the converted energy from the PV array would be wasted. Therefore, accurate monitoring of instantaneous peak power provides a basis for the power management strategy of the VRB storage system to achieve optimal utilization.

1.2 Objectives and Contributions

Although the VRB is a promising candidate for the energy storage, the related techniques are still not adequate to support its real commercialization, especially from the perspective of real applications. The accurate and robust monitoring of the key battery states is critical for the VRB to work safely and efficiently with an extensive calendar life. The major objectives of this study are summarized as follows:

- (1) A reliable battery model is the prerequisite of online battery state estimation and other electronic interfacing. The parameters of the battery model are commonly time varying with operating condition variation and battery aging thus online adaption is required. This study aims to propose an online adaptive battery model with high accuracy and low complexity which can be used for state estimate and any other control-orientated applications.
- (2) The peak power is an essential battery state reflecting the maximum power that can be drawn from or stored into the battery for the coming time intervals. This study aims to propose an equivalent circuit model (ECM)-based peak power estimation method to fully exploit the potential of VRB without violating the

safe operation limitations of battery.

- (3) The reliable SOC monitoring is essential to assess the battery condition and to avoid over-charge and/or over-discharge. This study aims to propose a data-driven based online SOC estimator which has high accuracy, high robustness, and low computational burden.
- (4) The capacity fade occurs as a consequence of different diffusion of vanadium ions across the membrane. The reliable monitoring of instantaneous capacity is essential for the diagnostic of the battery health condition. This study aims to propose a capacity estimator which can be implemented in real time without any constraint.
- (5) The measurement of current and voltage signals can be contaminated with non-ignorable noises in real applications, which may cause errors to the model identification and further the state estimate. This thesis also aims to investigate the effects of additive noises on model identification and state estimate. The thesis further seeks to explore an integrated framework to eliminate the noise effect and to realize the accurate model identification and SOC estimation.

With all the aforementioned objectives, systematic investigations are carried out to explore high-fidelity algorithms for the purpose of reliable and robust online state estimation. The major contributions of the thesis are summarized as follows:

- (1) This study adopts a common used ECM structure and explores online parameterization methods to make it adaptive and robust to the change of operating conditions and battery aging. The online identified battery model will be the basis for the model-based state estimate.
- (2) This study proposes an ECM based online peak power estimator. The estimator is formulated by considering multiple constraints, including voltage limit, SOC limit, and design current limit. A “two-step verification” method is designed to verify the proposed peak power estimator. The effect of prediction time horizon on peak power estimation is also investigated.
- (3) This study proposed a multi-timescale framework for model parameters and online SOC co-estimate. The model parameters and OCV are decoupled and estimated independently, effectively avoiding the possibility of cross

interference between them. Different timescales are adopted to enhance each estimator independently based on the analysis of model sensitivity, stability, and model accuracy.

- (4) This study proposes an online SOC and capacity joint estimation method. Except for the decoupling of model identification and state estimate, a novel EKF based joint estimator is formulated to estimate the SOC and capacity concurrently. The proposed joint estimator effectively compresses the filter order which leads to substantial improvement in the computational efficiency and numerical stability.
- (5) This study shows that the common model identification methods are intrinsically biased if the current and voltage sensors are corrupted with noises. To address this problem, a novel technique which integrates the Frisch scheme based bias compensating recursive least squares (FBCRLS) with a SOC observer is proposed to enhance the model identification and SOC estimate. The proposed method online estimates the noise statistics and compensates the noise effect so that the model parameters can be extracted without bias. The SOC is further estimated with improved accuracy based on the online updated battery model.

1.3 Organization of the Thesis

The thesis consists of seven chapters and three appendices, which have been organized as follows:

Chapter 1 briefly introduces the background of the study, including renewable energy and energy storage system, current research interests on VRB, battery management system, and online estimation of key states of VRB. The objectives and major contributions are also clarified.

Chapter 2 presents a detailed and in-depth literature review related to the research topics of this thesis. The chapter begins with the fundamental of the flow battery and further introduces the concept, features, comparison with other batteries, and current applications of VRB. Following that, special focus is given to several

essential aspects of BMS, including battery modeling, SOC estimation, capacity estimation, and peak power estimation. Existing methods concerning the aforementioned topics are introduced and compared in detail.

Chapter 3 introduces an online adaptive battery model for VRB and based on which an online peak power estimator is proposed. The first-order RC model is applied to simulate the battery dynamics and two identification methods, RLS and EKF, are used to online adapt the time-varying model parameters. Following that, an online peak power estimation method is proposed by accounting for multiple constraints, including voltage limitation, SOC limitation, and design current limitation. A “two-step verification” method is designed to verify the estimation accuracy. A hybrid pulse experiment is illustrated and the major constraints for different stages are discussed. The effect of the adopted prediction time horizon is also investigated.

Chapter 4 focuses on the online model parameters and SOC co-estimation for VRB with a novel multi-timescale estimator. The OCV and model parameters are fully decoupled and estimated with independent estimators to rule out the possibility of cross interference. Theoretical analysis on sensitivity, stability and precision are carried out to assess the performance of each estimator, based on which different timescales are used to enhance the co-estimation. Experiments on a lab-scale VRB system are conducted to verify the proposed method.

Chapter 5 presents the adaptive joint estimation of SOC and instantaneous capacity for VRB based on the online identified battery model. The computational efficient RLS is adopted to adapt the model parameters in real time. A simple OCV estimator which can be used for battery models with different orders is explored. The estimated OCV is treated as the noisy system measurement of an EKF based joint estimator for concurrent estimation of SOC and capacity. Experiments are carried out to show the fidelity and robustness of the proposed method. A comparison with another state-of-the-art method has also been done to highlight the superiority of the proposed method in terms of convergence speed, estimation accuracy, and computational cost.

Chapter 6 focuses on investigating the effect of noises on model identification and

SOC estimation. The existence of noises is shown to cause bias on model identification thus is detrimental for the model-based state observers. In order to attenuate the noise effect, a novel FBCRLS based observer is proposed to enhance the online model identification and SOC estimation. The noise statistics are online estimated to allow compensating the noise effect, in which the model parameters are extracted without bias. The SOC is further estimated with the online updated and unbiased battery model. Simulation and experimental results show that the proposed method is highly authentic. The comparison with existing methods highlights its superiority in terms of accuracy and convergence speed.

Chapter 7 summarizes the key conclusions of this thesis. Meanwhile, some potential research topics related to this thesis are recommended for the future work.

CHAPTER 2 Literature Review

2.1 Introduction

Secondary or rechargeable batteries as a group of chemical energy storage devices are among the leading EES technologies today. To date, they have already been widely used in many applications such as starting, lighting, and ignition (SLI) automotive applications, industrial truck materials handling equipment, emergency and standby power, and portable devices. Most recently, rechargeable batteries have received renewed interest as power sources for electric vehicles (EVs), hybrid electric vehicles (HEVs) and large-scale energy storage in a load leveling mode.

VRBs are promising candidates for the future energy storage systems (ESSs). They can be easily scaled up to formulate much larger storage capacities and show great potentials for the long lifetimes and lower per-cycle costs than the conventional batteries. In order to operate the VRB safely and efficiently with an extensive calendar life, a well-designed BMS is highly desired. In this chapter, a thorough literature review is carried out on the knowledge of VRB and the design of BMS including the battery modeling and the online estimation of the essential battery states.

The rest of this chapter is organized as follows. Section 2.2 briefly introduces the concept of redox flow battery (RFB) and its features compared with other secondary batteries. Section 2.3 reviews the knowledge of VRB in details, including the fundamental, features, comparison with other battery chemistries, and its applications to date. Section 2.4 provides in-depth review of the existing researches on the online state estimation techniques. The basic duty of BMS is briefed, following which the online estimation of SOC, instantaneous capacity, and peak power as the major topics of the thesis are comprehensively reviewed. The existing methods that are available in the open literatures and their associated advantages and disadvantages are discussed. Section 2.5 summarizes the current literatures and points out the existing challenges which will be extensively discussed and

addressed in the following chapters of the thesis.

2.2 Redox Flow Battery

Redox flow batteries (RFBs) are also viewed as electrochemically regenerative fuel cells because they involve the supply of an externally stored fuel and oxidant in the form of soluble redox couples that produce the electrical energy when undergoing the oxidation and reduction reactions [16]. Energy is stored chemically in the two electrolytes containing different redox couples. The electrolytes are pumped from each tank into the flow cells across a proton exchange membrane where one form of the electrolyte is electrochemically oxidized while the other is electrochemically oxidized.

Compared with other secondary batteries, the undesirable electrode processes like the structural changes are eliminated by using the fully soluble redox couples and inert electrodes. The battery capacity is determined by the volume of external reservoirs and the concentrations of the reactants, while the battery power is determined by the number of individual cells within a battery stack and their electrode areas. As such, the capacity and power can be designed and optimized independently with high flexibility when facing a specific application. The capacity can be enlarged by simply using more electrolytes or higher reactant concentration, so that the cost of scale-up is much lower than that of other batteries. Another important advantage is the flexibility during charge/discharge cycles, i.e. the RFB can be completely discharged without damaging the cells permanently [17]. The main disadvantage of RFB is that the electrolytes are made of different substances and separated by a membrane that is permeated inevitably. The two electrolytes can mix with each other and further render the battery useless, which is called the cross contamination.

2.3 Vanadium Redox Flow Battery

2.3.1 Fundamental

The research on the VRB began in 1984 at the University of New South Wales. The VRB was pioneered by Skyllas-Kazacos [7] and co-workers to overcome the inherent problem of RFB, i.e. the cross contamination by diffusion of different redox ions across the membrane. As a significant advancement, the VRB employs the same element in both half-cells to eliminate any cross contamination phenomenon, so that allows the electrolyte life to be extended indefinitely [18].

The VRB employs four different vanadium valences species in both sides. The V^{2+}/V^{3+} and V^{4+}/V^{5+} redox couples in sulphuric acid are employed respectively for negative and positive half-cells with the following charge-discharge reactions:

Positive electrode reaction:

Negative electrode reaction:

where SHE stands for the standard hydrogen electrode. The OCV of the above mentioned redox couples is about 1.6 V when the positive and negative half-cell electrolytes comprising 2 mol/L V^{5+} and 2 mol/L V^{2+} respectively. The system can be operated over a temperature range of 10 - 40°C without safety issues.

The schematic diagram shown in Figure 2.1 describes how the VRB is functioned and operated. As shown, the charge and discharge reactions happen on the surface of the solid electrodes and accordingly generate the electrical potential. An ion exchange membrane separates the two half electrolytes which allows only protons to transfer between cells so that the active reactants cannot mix. Different from

other secondary batteries, the electrolytes are stored externally in two independent tanks, and are circulated through the cells with two pumps. The maximum amount of energy that can be stored in VRB is determined by the concentration of the vanadium species in each electrolyte and the volume of the electrolytes.

Figure 2.1 Schematic diagram of a redox flow battery with electron transport in the circuit, ion transport in the electrolyte and across the membrane, active species crossover, and mass transport in the electrolyte

Figure 2.2 VRB structure: (a) prototype of a 10W VRB cell; (b) schematic of stack structure of VRB

By compressing numbers of single-cells together, a stack as the most essential component of VRB can be formulated. The formulation decides the output power of

VRB. The stack is composed of serial connected single-cells with two solid electrodes in contact with the liquid electrolytes and the current collectors. A scale-up system can be achieved by increasing the area of the electrodes, adding more electrolytes in the tanks or by connecting the stacks in either series or parallel configurations. The prototype of a lab scale 10W VRB is shown in Figure 2.2 (a). Figure 2.2 shows the schematic of a stack structure in the VRB.

2.3.2 Features

The VRB has been the most studied redox flow cell and also commercialized for some applications for its unique advantages compared with other electrochemical energy storage technologies. The advantages of VRB are summarized as follows:

(1) Capacity/power independence

The VRB stores the chemical energy in the form of two vanadium electrolytes contained in two independent reservoirs. Therefore, the battery capacity can be easily enlarged by simply adding more electrolytes, which is quite cost efficient compared with the scale up of other battery systems. Otherwise, the output power of VRB is determined totally by the electrode area and the number of single cells connected in series or parallel, indicating that the design of the power and capacity of VRB are separated and highly flexible according to the practical requirements.

(2) Cross-contamination elimination

The VRB applies vanadium solutions in both half-cells. The use of a single-metal system makes it free from the problem of cross-contamination caused by the transfer of ions across the membrane as well as any problems associated with the use of pre-mixed solutions.

(3) Fast charging

The “empty” battery can be immediately fully charged by simply replacing the spent electrolytes. Such advantage will be of particular interest for the applications in electric cars as it allows the rapid refueling by electrolyte exchange at the special refueling stations. As such, the slow charging time associated with conventional battery technologies can be avoided while the

spent electrolytes can be recharged during the periods of low demand [19]. Progresses with the hybrid redox fuel cells lead to significant improvements in the energy density which will further facilitate the applications in electric vehicles.

(4) High tolerance to over-charge and over-discharge

The VRB is highly tolerant to the over-charge and over-discharge within the limits of the capacity and current density. It can also be cycled from any state of charge without permanent damage to the cells or electrolytes [20]. However, it has to be pointed out that the high tolerance to over-charge and over-discharge is relative to the other battery chemistries. In real applications, the VRB is not recommended for over-discharge and especially over-charge. No morphological changes that limit the depth of discharge are observed to date, and the only consequence of over-discharge is the cell reversal. In contrast, the effect of over-charge is more complicated. Gassing side reactions will occur at both half-cells and cause fading of capacity especially during the charging process [13]. Specifically, the hydrogen evolution at the negative half-cell is significant above 90% SOC. Severe over-charge conditions can also deteriorate the electrode materials. For example, the over-charge will lead to the oxidation of the carbon black materials used in the bipolar electrode substrate which further causes the increase of resistance. The oxidation of graphite felt materials will form the carbon/oxygen functional groups which are removable under reducing conditions. However, the oxidation of the more reactive carbon black filler material can lead to CO₂ formation resulting in delamination and destruction of the composite matrix. As a result, although the tolerance of VRB to over-charge and over-discharge is high, they are better to be avoided in real applications.

(5) Easy thermal management

The electrolytes are circulated with the external loops, so that the thermal management system can be easily designed with either the natural cooling or the forced cooling techniques.

Other major advantages include the low capital cost, the long life cycle, the high energy efficiency, and the low toxicity, etc.

2.3.3 Comparison with Other Battery Chemistries

It is of great importance to compare the battery characteristics and the cost aspects of different battery techniques, as they are critical to the introduction of large scale ESSs when evaluating the suitability of batteries for grid operation. Apart from the VRB, other typical battery techniques include the lead-acid battery, the lithium-ion battery, the sodium-sulfur, and the nickel-based batteries. Nowadays, the use of nickel-based batteries is diminishing as a consequence of the high cost. The various characteristics, costs, and maturities have been summarized in Table 2.1 for comparison. It is observed that the VRB has superiority in the cycling life, self-discharge rate, system level cost, and total life time.

The lithium-ion battery is a promising technique that shows many merits and has been widely applied in many fields like portable electronics, transportation electrification, and grid construction. Relatively speaking, as shown in Table 2.1, the lithium-ion battery has the characteristics of high cycle life, high energy density, high power density, high efficiency, and low self-discharge rate. However, the complex control circuitry is required to avoid the over-charge which results in overheating and failure immediately. The high efficiency enables large charge and discharge currents, but this increase the risks associated with overcharging. Moreover, the battery pack should incorporate numbers of cells in series and parallel. The balance between each cell requires reliable control algorithm and circuitry which are quite challenging and somewhat expensive, pushing the cost of an already expensive battery even higher.

By comparison, the VRB has very long cycling time and negligible self-discharge which are all favorable for real applications. One outstanding feature of VRB is that the capacity can be increased by simply adding more electrolytes, so the theoretical capacity can be infinite. The incremental cost of each additional energy storage capacity unit is much lower than other types of battery. For this reason, the cost per kWh of the system decreases substantially with increasing storage capacity, making the VRB particularly attractive for the large-scale applications. Moreover, all the battery stacks in series or parallel can be feed with electrolytes from the same external reservoir, thus the balancing problem associated with the lithium-ion

battery can be well eliminated. Some other unique advantages of VRB over the lithium-ion battery, such as the independence of capacity and power design, fast charging, high tolerance to over-charge and over-discharge, and easy thermal management are not repeated here. The only concern about VRB is the low power and energy density. The VRB system should be very large in size in order to fulfil the requirement on rated power and energy, which limits its usage in the field of electrical mobility such as EVs and HEVs. However, this is not an issue for the stationary energy storage application where the space is not the main concern.

2.3.4 Applications

To date, the VRB has shown the greatest potential for the applications of large-scale energy storage with high energy efficiencies over 80% and meanwhile long cycling life. This battery technique has been applied in the MW- and kW-scale projects with practical demonstrations covering a range of stationary and mobile applications in Japan, China, Europe, Australia and the USA. Except for the merit of cross contamination elimination, the VRB also shares a considerably low cost for large-scale storage. As discussed, the cost per kWh substantially drops when the capacity is enlarged. The projected costs for eight or more hours of storage are typically as low as US\$150/kWh. The representative applications of VRB are summarized in the following texts.

In 1993, Mitsubishi Chemicals and Kashima-Kita Power Corporation of Japan licensed the VRB technology for stationary usage. The technology was scaled up for the purposes of load-leveling and solar energy storage applications [21]. After that, a 3 m³/day electrolyte production plant was commissioned in early 1996.

In 1997, the 200 kW/800kWh grid connected VRB was commissioned at the Kashima-Kita Electric Power station in Japan. The long-term testing which consisted of 150 charge-discharge cycles showed a high energy efficiencies of close to 80% [21].

Table 2.1 Characteristics of different battery technologies

Battery type	Lithium-ion		Lead–acid		Sodium–sulfur	VRB
	Power cell	Energy cell	Power cell	Energy cell		
Cycle life	3000	3000+	50 to 200	200 to 1800	210 to 4500	5000 to 14000
Energy density (Wh/kg)	75 to 200	75 to 200	30 to 50	30 to 50	150 to 250	10 to 30
Power density (W/kg)	2400	75 to 300	300	75	150 to 230 possible, commercial up to 30	N/A
E/P ratio (kWh/kW)	0.025 to 0.075	0.27 to 0.6	0.13	0.5	6	1.5 to 6+
Self-discharge per day	0.1% to 0.3%	0.1% to 0.3%	<0.5%	<0.5%	20%	Negligible
Cycle efficiency	80 to 98%	80 to 98%	63 to 90%	63 to 90%	75 to 90%	75 to 85%
Format	Cylindrical	Prismatic	Cylindrical	Prismatic	Tall cylindrical	Separate tanks
Active material phase	Solid	Solid	Solid	Solid	Liquid	Liquid
System level cost (US\$/kWh)	600 to 1200	600 to 1200	200 to 600	200 to 600	300 to 950	150
Life time (years)	5 to 10	5 to 10	5 to 10	5 to 10	5 to 10	>10
Maturity level	Commercial	Commercial	Mature	Mature	Commercializing	Developed
Modular	Sealed, modular	Sealed, modular	Modular	Modular	High temperature	Liquids
Safety issues	Potential fires and explosions		Potential for hydrogen explosions		High temperature operation	Chemical leakage

Since 1999, more than 20 VRB demonstration systems were carried out by Sumitomo Electric Industries. The applications included load leveling, wind energy storage, and emergency back-up power. The energy efficiencies were maintained at 80% and up to 270,000 charge-discharge cycles had been committed [22].

From 2001 to 2005, several more applications were undergone. A 250 kW/520 kWh VRB based energy storage system (ESS) was established in South Africa. A 250 kW/1 MWh VRB system was installed for Hydro Tasmania in Australia for wind energy storage and diesel fuel replacement. A 250 kW/2 MWh VRB was installed in the USA by VRB Power for voltage support and rural feeder augmentation. Sumitomo Electric Industries installed a 4 MW/6 MWh VRB system at Subaru Wind Farm for the aim of wind energy storage and wind turbine output smoothing.

A VRB powered electric golf cart was field tested at UNSW to show its potential for mobility applications. The testing result suggests that the energy density of VRB approaches that of lead-acid, with the unique advantage of rapid recharging by the electrolyte replacement. Subsequent tests with a 3 M vanadium electrolyte showed that a driving range of 54 km could be achieved if the tanks were filled.

The research on VRB was initiated in China by Zhang and co-workers at the Dalian Institute of Chemical Sciences. A 1 kW stack was designed in 2006 and further several stack modules were integrated into a 10 kW VRB system with 4 modules in series and 2 in parallel [23]. The overall energy efficiency was tested to be more than 80%.

In 2009, Zhangbei storage building as China's first comprehensive demonstration project was launched by Chinese National Grid. A total of 75 MW of projects were demonstrated in the energy storage including the VRB, the lithium-ion battery, and the sodium-sulphur batteries. Among them, the VRB was found desirable for the wind energy storage [24].

In 2010, the US Department of Energy funded the application of a 1 MW/8 MWh VRB system to facilitate the load leveling at the Painesville Municipal Power Station in Ohio. This project also intended to include the development of 10 - 20

kW systems for the batch production.

In 2012, the demonstration power plant of the Woniushi wind farm was launched by the Chinese National Grid. The VRB was applied for the wind storage. The whole system was configured by five 1 MW VRB modules each with a rated output power of 22 kW. In 2013, the demonstration power plant was successfully connected to the grid for transmission.

2.4 Online State Estimation Techniques

The VRB is a promising candidate for the future energy storage market. However, the related techniques are still not adequate to support its real commercialization. Lots of key issues linking the chemistries to real applications are to be addressed. In this regard, a well-designed BMS with high reliability is pivotal to operate the VRB safely and efficiently with an extensive calendar life.

The BMS is an embedded system that incorporates the purpose-built electronics and processing to guarantee the safe and efficient operation with a long calendar life. A BMS requires both hardware (electronics) and software (algorithm) components. The hardware part adopts electronic circuits to measure the current, voltage, and temperature and to ensure the safe operation. The software parts rely on the advanced computing algorithms to monitor and coordinate the activities of battery.

In this thesis, we only focus on the software part of BMS. The major aim is to implement mathematical methods by using the onboard measured signals to estimate and summarize the present operating status and to forecast the near-future performance limits.

As a key component in the battery systems, the BMS should be able to execute the performance managements including estimating the SOC, computing the battery available energy and the peak power. Additionally, the BMS should also be able to make diagnostics to estimate the SOH. In this section, an overview of these requirements is presented.

2.4.1 What to Be Estimated

To make short-term and long-term plans for energy management, two fundamental battery states should be known: How much remaining energy is available in the battery and how much power can be outputted from or inputted into the battery in the future. This calls for the reliable monitoring of SOC, capacity, and peak power. Ideally, it is expected to measure and feedback these values directly; however, no sensors can measure these kinds of internal states. For this reason, it is demanded to estimate these values based on the basically measured signals like current, voltage and temperature.

The present SOC and total capacity are indispensable to calculate the remaining energy in the battery. It should be noted that SOC itself is a critical index to avoid over-charge and over-discharge. Too high SOC will cause gassing side reactions which will lead to imbalance of active species in the two half-cells, and finally results in significant capacity fade and battery aging. Moreover, too high SOC can also lead to the oxidation of the electrode materials and cause increased internal resistance. In contrast, over-discharge can lead to cell reversal which deteriorates the cell performance. The estimate of peak power depends on a battery model with accurate model parameters. The incorrect estimation of peak power may cause the current or voltage to break the design limits and further may lead to severe safety issues. The logic of online state estimation is shown schematically in Figure 2.3. The poor estimation algorithms may lead to less accurate results and the impact of which will be rather expensive.

Figure 2.3 Schematic diagram of online state estimation

2.4.2 Battery Modeling

As the variables like SOC, SOH, and peak power are not directly measurable by any sensors, they need to be estimated, commonly from the model-based estimation algorithms. Within this context, an accurate battery model which precisely reproduces the battery dynamics is the prerequisite of the model-based state estimators. However, the electrochemical reactions inside the battery are rather complicated with nonlinear behaviors. Apart from the main electrochemical reactions, there also exist some unexpected side reactions, such as corrosion and self-discharge. The battery is thereafter a highly nonlinear system. The dynamical behavior depends on different variables and difficult to grasp. For this reason, the investigation of reliable battery models should be carefully addressed. In addition to providing accurate estimations, it is paramount to strike a balance between accuracy and model complexity to allow the models embedded in microprocessors. In other words, the model is desired to be accurate enough while not unnecessarily complicated. Generally, the battery models can be categorized into three groups, i.e. electrochemical model, computational intelligence based black-box model, and the equivalent circuit model (ECM).

A. Electrochemical model

To date, most of the existing models for VRB are the so-called electrochemical models [25-31] which typically deploy coupled partial differential equations (PDEs) with a large amount of unknown parameters. Such models describe the ion transport phenomena and the dynamic process of distributed electrochemistry reactions occurring in the electrodes and electrolyte.

Walsh et al. at the University of Southampton established the first electrochemical model of VRB [25]. The proposed two-dimensional model comprehensively describes the mass, charge, momentum transport and conservation, and the global kinetic model for electrode reactions. This model can be used to study the effects of a broad range of design parameters including ion concentration, electrolyte flow rate, and electrode porosity on the performance of the battery. Following that, an extension study on the non-isothermal model was established to explore the effect

of operating temperature on battery performance [26]. The results show that both the charge-discharge characteristics and the temperature distribution are notably influenced by the operating flow rate and current density. Further, the oxygen evolution at the positive electrode and hydrogen evolution at the negative electrode were taken into account and incorporated into the model [27, 28]. The modeling was performed to study how the operating temperature, flow rate, current density, and bubble diameter affect the extent of oxygen and hydrogen evolution. Zhang et al. at Dalian Institute of Chemical Physics comprehensively studied the effects of current density, local mass transfer coefficient, and electrode porosity on the performance of the battery [29]. A three-dimensional model for the negative half-cell was built based on which the effects of electrolyte flow rate are investigated [30]. A two-dimensional time-dependent single-phase isothermal model was established for a single cell, suggesting that the fluid mechanics decouples from the electrochemistry [31].

The advantages of the electrochemical models are summarized as follows:

- (1) The models can achieve high accuracy for the detailed characterization of inner physiochemical process.
- (2) The models have the merit of ensuring each model parameter to retain a specific physical meaning.
- (3) The models clearly show the dependence of battery performance on a list of environmental and design conditions.

Due to the advantages, the electrochemical models are suitable for understanding the distributed electrochemistry reactions in the electrodes and electrolytes. They are also of great significance for predicting cell performance, improving the membranes and flow field design, and optimizing the key operating variables such as current density and temperature. However, when considering their applications in online computing or control of interfacing electronics, the electrochemical models are not adequate. The major drawbacks of them are listed as follows:

- (1) The high computational complexity leads to a significant requirement for the memory and computation, thus prohibits them from being used on the low-

cost microcontrollers. Model simplification or reduction should be conducted for control and estimation purposes.

- (2) The robustness of the model is questionable in real applications as it is impossible to adapt all the model parameters, most of which are empirical, to the change of operating conditions.
- (3) Extensive investigations are demanded as they require detailed understanding of the battery, such as the kinetic reactions that take place as well as the material properties.
- (4) The large amount of model parameters may cause significant over-fitting issues [32]. The model parameters are often unavailable. The tuning of model parameters also depends highly on the researchers' experience in electrochemical reactions and detailed knowledge of the system.

Consequently, as suggested by Sharkh et al. [33] and Dees et al. [34], the electrochemical models are more proper to be used for battery physical design and optimization of electrodes and electrolytes. Modern advanced management and control rely on a battery model that should be dynamic, adaptive, and robust.

B. Computational Intelligence based Model

The computational intelligence based methods view the battery as a black box and adopt the machine learning techniques like the artificial neural network (ANN) and support vector machine (SVM) to approximate the highly nonlinear battery dynamics. As an instance, the ANN can build up a neural architecture which is usually composed of the input layer, the hidden layers and the output layer to approximate the dynamic properties of the battery. Such models were extensively attempted on the lithium-ion battery, lead-acid battery, and sodium-sulfur battery but have not been reported to be applied on the VRB yet. The computational intelligence based models demand no exact knowledge of the battery structure or dynamics, thus bring significant convenience to the engineers without much knowledge on electrochemistry.

Charkhgard et al. [35] used a radial basis function neural network (RBFNN) battery model based on which an adaptive filter was applied to infer the SOC. Xu et al. [36]

adopts the stochastic fuzzy neural network (SFNN) to build the battery model in order to attenuate the effect on noisy input. For the past few years, ANN that can approximate any nonlinear function in arbitrary precision has been proved. However, the generalization performance of ANN is unsatisfactory, which is supposed to be the reason of local minimum especially in small sample conditions. By comparison, the SVM is a kind of supervised learning method based on the structure risk minimization and has been shown to have good generalization ability. Wang et al. [37] proposed a SVM-based battery model by using the load current, temperature and SOC as the model inputs and the terminal voltage as the model output. The aforementioned models use the offline trained model without adaption during the battery working cycle. The robustness of them is doubtful if the operating conditions change or battery degrades. As an improvement, Meng et al. established a battery model based on the least square support vector machine (LSSVM). The developed LSSVM model is continuously updated online with the recently obtained sampling data during the battery operation, in seeking to adapt to the changes of battery internal characteristics and also operating condition after a period of operation.

The main disadvantages of the computational intelligence based models are:

- (1) The training process of the model is too complex. Lots of factors have to be considered, like the type of transfer functions, the number of hidden neurons, the number of hidden layers, the weight and threshold. The model training demands a large amount of data and also requires a long processing time, thus its suitability for real embedded system is still questionable.
- (2) The robustness of the model is not verified. The models are commonly trained by offline data set and can work accurately for the present period. With the continuous operation of the battery, however, the model may lose accuracy as both the battery state and the operating conditions change.
- (3) An appropriate activated function which correctly reflects the correlation between the activated states and the output of neurons have to be prescribed empirically based on a large training data set, which can lead to significant over fitting [38].

C. Equivalent Circuit Model

The ECMs use a combination of the SOC-dependent voltage source, resistors, capacitors, and possibly the nonlinear elements such as the Warburg impedance to form a circuit network to approximate the battery dynamics. Typically, an ideal voltage source is selected to describe the OCV, while the remainder of the circuit simulates the battery's internal resistance and the polarization effects. As a physical analogy exists between the ECM components and the actual battery, this category of models are often called the gray box models. The circuit representation of ECMs is computationally easier and meanwhile provides reasonable accuracy. The excellent adaptability and easy realization of ECMs will be of interests to the design and control of interfacing electronics. In this section, we will review the commonly used ECMs for a broad range of battery chemistries, rather than only constrained within the range of VRB.

The ECMs are commonly lumped models with a fewer number of model parameters compared with the electrochemical models. Plett [39] proposed several lumped models, including the combined model, the simple model, the zero-state hysteresis model, the one-state hysteresis model, and the enhanced self-correcting (ESC) model. The battery models and the corresponding characterization equations are summarized in Table 2.2. Comparison results show that although the combined model perform well, the model parameters over-fit the measured data; consequently the model does not resemble OCV to any degree of fidelity. In contrast, the simple model yields a lower accuracy but it generalizes better than the combined model. A performance jump is observed by taking the hysteresis into account, and adding the dynamics of states into the hysteresis model further improves performance. Further performance enhancement can be expected by increasing the number of filtering states but at the cost of improving computational complexity.

The resistance-capacitance (RC) network based ECMs, such as the Rint model, the Thevenin model (first-order RC model), the dual polarization (DP) model (second-order RC model) and their revisions were also widely studied [32]. Four representative RC networks based ECMs are shown schematically in Figure 2.4, and their corresponding descriptions are summarized in Table 2.3.

Table 2.2 Details of the existing equivalent circuit models: part 1 [39]

Model	Characterization equations and description
The combined model	$s_{k+1} = s_k - \eta I_{L,k} t_s / Q_k$ $V_{t,k} = K_0 - K_1 / s_k - K_2 s_k + K_3 \ln(s_k) + K_4 \ln(1 - s_k) - I_{L,k} R_s$ <p>where $I_{L,k}$, $V_{t,k}$, and s_k are the load current, terminal voltage, and SOC; η is the coulombic efficiency; t_s is the sampling time interval; Q is the capacity; K_0, K_1, K_2, K_3 and K_4 are the model coefficients for the correlation between OCV and SOC; and R_s is the ohmic resistance.</p>
The simple model	$s_{k+1} = s_k - \eta I_{L,k} t_s / Q_k$ $V_{t,k} = V_{oc}(s_k) - I_{L,k} R_s$ <p>where $V_{oc}(s_k)$ represents the OCV which is obtained using the SOC-OCV look-up table.</p>
The zero-state hysteresis model	$s_{k+1} = s_k - \eta I_{L,k} t_s / Q_k$ $V_{t,k} = V_{oc}(s_k) - I_{L,k} R_s - \mathcal{G}_k M,$ $\text{where } \mathcal{G}_k = \begin{cases} 1; & I_{L,k} > \xi \\ -1; & I_{L,k} < -\xi \\ \mathcal{G}_{k-1}; & I_{L,k} \leq \xi \end{cases}$ <p>where M is the hysteresis level which is a constant coefficient, and ξ is an adequately small and positive threshold.</p>

The one-state
hysteresis model

$$\begin{bmatrix} h_{k+1} \\ s_{k+1} \end{bmatrix} = \begin{bmatrix} \exp(-|\eta I_{L,k} \kappa t_s|) & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} h_k \\ s_k \end{bmatrix} + \begin{bmatrix} 0 & 1 - \exp(-|\eta I_{L,k} \kappa t_s|) \\ -\eta t_s / Q_k & 0 \end{bmatrix} \begin{bmatrix} I_{L,k} \\ M(s, \dot{s}) \end{bmatrix}$$

$$V_{t,k} = V_{oc}(s_k) - I_{L,k} R_s + h_k$$

where h_k is the hysteresis voltage; κ is the rate of decay; and M is the maximum polarization due to hysteresis as a function of SOC and the change rate of SOC. Specifically, $M(s, \dot{s})$ is positive for charging ($\dot{s} > 0$) and negative for discharging ($\dot{s} < 0$).

The enhanced
self-correcting (ESC)
model

$$\begin{bmatrix} f_{k+1} \\ h_{k+1} \\ s_{k+1} \end{bmatrix} = \begin{bmatrix} \text{diag}(\alpha) & 0 & 0 \\ 0 & \exp(-|\eta I_{L,k} \kappa t_s|) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} f_k \\ h_k \\ s_k \end{bmatrix} + \begin{bmatrix} 1 & 0 \\ 0 & 1 - \exp(-|\eta I_{L,k} \kappa t_s|) \\ -\eta t_s / Q_k & 0 \end{bmatrix} \begin{bmatrix} I_{L,k} \\ M(s, \dot{s}) \end{bmatrix}$$

$$V_{t,k} = V_{oc}(s_k) - I_{L,k} R_s + h_k + g f_k$$

where f is the state vector of a low-pass filter of the current; α is the state-transition matrix of the filter; g is the output matrix of the filter and a zero-dc gain constraint is applied to it.

Figure 2.4 Schematic diagram of RC network based ECMs: (a) The Rint model; (b) The Thevenin model; (c) The first-order RC model with one-state hysteresis; (d) The DP model

The Rint model [40] is very simple in the model structure with only one nonlinear voltage source in series with the internal ohmic resistance. However, the transient dynamics and hysteresis are ignored thus the model is not adequate in the dynamic current excitation conditions.

Based on the Rint model, the Thevenin model adds one parallel RC network to simulate the transient effect. The Thevenin model has been one of the most popular models that are widely applied in open literatures for its simple structure and the reasonably high accuracy [41-51]. Hu et al. [52] compared twelve typical ECMs and concluded that the Thevenin model was the best trade-off between the model complexity and accuracy and was a good candidate for online applications. Dedicated elements depicting the battery hysteresis behavior were added to the RC based ECMs, such as the first-order RC model with hysteresis [53-55]. Such models improve the accuracy to some extents but at the cost of higher computational complexity.

Table 2.3 Details of the existing equivalent circuit models: part 2

Model	Characterization equations and description
The Rint model	$s_{k+1} = s_k - \eta I_{L,k} t_s / Q_k$ $V_{t,k} = V_{oc}(s_k) - I_{L,k} R_s$
The Thevenin model (first-order RC model)	$s_{k+1} = s_k - \eta I_{L,k} t_s / Q_k$ $V_{p,k} = \exp\left(-\frac{\Delta t_s}{R_p C_p}\right) V_{p,k-1} + \left[1 - \exp\left(-\frac{\Delta t_s}{R_p C_p}\right)\right] R_p I_{L,k-1}$ $V_{t,k} = V_{oc}(s_k) - I_{L,k} R_s - V_{p,k}$ <p>where $V_{p,k}$ is the polarization voltage across the RC network; and R_p and C_p are the polarization resistance and capacitance, respectively.</p>
The first-order RC model with one-state hysteresis	$s_{k+1} = s_k - \eta I_{L,k} t_s / Q_k$ $V_{p,k} = \exp\left(-\frac{\Delta t_s}{R_p C_p}\right) V_{p,k-1} + \left[1 - \exp\left(-\frac{\Delta t_s}{R_p C_p}\right)\right] R_p I_{L,k-1}$ $h_{k+1} = \exp\left(- \kappa I_{L,k} \Delta t \right) h_k + \left[1 - \exp\left(- \kappa I_{L,k} \Delta t \right)\right] H$ $V_{t,k} = V_{oc}(s_k) - I_{L,k} R_s - V_{p,k} + h_k$ <p>where $V_{oc}(s_k)$ represents the OCV as a function of SOC.</p>
The DP model (second-order RC model)	$s_{k+1} = s_k - \eta I_{L,k} t_s / Q_k$ $V_{p1,k} = \exp\left(-\frac{\Delta t_s}{R_{p1} C_{p1}}\right) V_{p1,k-1} + \left[1 - \exp\left(-\frac{\Delta t_s}{R_{p1} C_{p1}}\right)\right] R_{p1} I_{L,k-1}$ $V_{p2,k} = \exp\left(-\frac{\Delta t_s}{R_{p2} C_{p2}}\right) V_{p2,k-1} + \left[1 - \exp\left(-\frac{\Delta t_s}{R_{p2} C_{p2}}\right)\right] R_{p2} I_{L,k-1}$ $V_{t,k} = V_{oc}(s_k) - I_{L,k} R_s - V_{p1,k} - V_{p2,k}$

The DP model adopts two RC networks to refine the Thevenin model [56-58]. The two RC networks are used to simulate the transient processes with different time constants, which are commonly seen in most battery chemistries. Mohamed et al [59] built a DP model for the VRB using the EKF for parameterization. The two RC networks were used to simulate the activation polarization with a small time constant and the concentration polarization with a relatively large time constant.

Theoretically speaking, the DP model is more accurate than the Thevenin model as the separation of transients with different timescales will make better sense to refine the modeling of dynamics. The drawback is that the model complexity will lead to a high computational cost and a high numerical instability for model identification.

D. Equivalent Circuit Model for VRB

Till now, only a few publications can be found concerning ECMs applied to the VRB. Chahwan et al. [60] proposed a simple ECM to obtain the energy content and terminal voltage profile of VRB, aiming to study its application in power systems. The proposed simple ECM was used for the stand-alone wind energy system simulation and grid-connected wind farm power control [61-63]. Qiu et al. [15] further simplified the model and utilized it for the controller design of a microgrid with photovoltaic. Later, the simple model was extended to incorporate the environmental controls by the heating, ventilation, and air conditioning system to provide a more realistic efficiency profile [64]. The simple ECM and its variants introduce the system losses such as pump loss and parasitic loss which are quite insightful for the VRB study; however, they are aimed for system simulation where the requirement on modeling accuracy is not high. The losses are also estimated empirically without detailed explanations. Moreover, the models have not been verified with the real experimental data.

In recent years, multiple ECMs for VRB with new structures have been reported. Ontiveros et al. [65] used a simplified circuit model with only the equilibrium potential and the ohmic resistance for power system dynamic studies. Wei et al. [66-68] integrated the thermal model into the ECM to ensure the model fidelity over a wide range of operating conditions. Zhang et al. discussed a comprehensive ECM by taking the transient process, shunt current and vanadium iron diffusion into account [69]. One common drawback of these models is that the model parameters which are crucial for modeling accuracy are determined empirically without a detailed method for identification. In order to tackle this problem, Mohamed et al. [59] proposed to use the second-order RC model for VRB and adopted the EKF to identify the model parameters. The dynamics of VRB including the activation polarization and the concentration polarization are modeled separately. Seven state

variables are included in the transition and the result shows a satisfactory modeling accuracy. The seventh-order EKF, however, will cause the extensive calculation of the high-dimension matrices which is quite computational heavy and not easy to be implementable for online applications. The high order filter may also be subject to instability issues. Despite the drawbacks, such an online adaptive model will open-up feasibility studies for the VRB applications such as EV and HEV.

2.4.3 SOC Estimation

There is no uniformly accepted definition of SOC. Throughout this thesis, the SOC is defined as the remaining capacity as a percentage of the total capacity when the battery is fully charged under the same standard condition. The determination of SOC is quite important in BMS. The incorrect information on SOC may cause over-charge or over-discharge and lead to irreversible reduction in the battery lifetime. To date, several methods have been reported in the open literatures to monitor the battery SOC. In this section, some methods for a broad range of battery chemistries and specifically intended for VRB will be systematically reviewed.

A. Coulomb Counting

The coulomb counting (CC) method is viewed as the most simple and standard method to obtain the battery SOC if the initial state is well known and the sensors are of high precision. The CC technique can be expressed as:

$$s(t) = s(t_0) - \frac{1}{Q} \int_{t_0}^t \eta I_L dt \quad (2.3)$$

where t_0 denotes the initial time when the SOC is known.

The CC method has quite satisfactory precision within a certain period of time of the initial SOC is known or can be estimated properly. It is suitable for online applications for the following reasons:

- (1) The method demands only the low-cost sensors for current measurement.
- (2) The computational burden is very low thus is implemental in low-cost

processors.

- (3) It is easy to be combined with other techniques.

The main disadvantages are:

- (1) The initial SOC cannot be known in real applications, causing the method to lose effectiveness.
- (2) The method is intrinsically an open-loop method. When performed over a long period of time, errors caused by current noise or drifting will accumulate and the method lacks a close-loop feedback mechanism for correction.

Therefore, the SOC estimation results of applying only the CC method cannot meet the requirement on precision. Otherwise, it is used commonly in combination with other supporting techniques, for example with an OCV-based SOC estimator.

B. OCV Based Method

There is a correlation between SOC and OCV, and this correlation changes very little along with the battery aging process. Accordingly, it is an effective method to estimate the SOC by measuring the OCV of battery. For the power batteries, it should be mentioned that the temperature effect on the SOC-OCV correlation should be considered as the batteries work within a large temperature range. Therefore, the OCV should be considered as a binary function of both SOC and temperature and a three-dimensional look-up table is used to estimate the SOC from the measured OCV and temperature. In contrast, the working temperature of VRB is constrained between 10°C and 40°C in order to prevent the thermal precipitation of the vanadium species. Within the narrow temperature range, the SOC-OCV variation caused by temperature is very limited and thus can be ignored. Therefore, the SOC determination of VRB is easier by inferring directly from the measured OCV.

The greatest advantage of the OCV method is the high accuracy and the feasibility with only voltage sensor. Additionally, the SOC-OCV relationship changes only slightly over the battery lifetime thus no frequent recalibrations are needed. The remarkable disadvantage when applied to most secondary batteries like the lithium-

ion is that the battery is required to have long time resting in order to reach the actual Electromotive Force (EMF) value. Sometimes the battery has to be used very frequently and there might be only short periods of time to allow measuring the battery OCV. Under this condition, the measured OCV might be “disturbed” by the significant overvoltage which declines slowly after current interruption.

The flow batteries allow the use of open circuit cells to measure the OCV directly and immediately without the need to relax the battery for a sufficiently long time. This is a unique advantage of VRB by comparison with other batteries regarding the online SOC determination. The only drawback of this method is that additional open circuit cells and sensors have to be installed and thus increase the complexity of battery configuration.

C. Electrochemical Based Methods

The alternating current (AC) impedance method [70-72] and the direct current (DC) internal resistance method [73] have also been used for SOC determination. The AC impedance method loads a series of small amplitude sinusoidal alternating currents with different frequencies to the battery. The frequency responses under different frequencies are measured and further the SOC can be obtained through the analysis of AC impedance. The DC internal resistance method calculates the internal resistance of battery with a fixed time interval. Since the DC internal resistance has certain correspondence to the SOC, based on which the SOC can be inferred. These methods are limited for online applications considering the following reasons:

- (1) An additional signal generator is required to apply the AC impedance method, which leads to an increase in cost and prohibits it from online applications.
- (2) The relationship between the SOC and AC impedance or DC resistance is complicated and easily affected by many factors.
- (3) Under the condition that the impedance changes little for a wide SOC range, the SOC estimation, if possible, will incorporate large errors.

To date, there have been some methods published in regard with the SOC monitoring specifically for the VRB. The measurement of electrolyte conductivity

and spectrophotometric properties were proposed by Kazacos and Skyllas-Kazacos to determine the battery SOC under the lab testing conditions [74]. The hydrogen ion concentration will gradually increase as the SOC increases; as a consequence an increase in the conductivity in both the half-cells is expected to be observed. In addition, different vanadium oxidation states show different colors as: V^{2+} (violet), V^{3+} (green) and V^{4+} (blue), V^{5+} (yellow). The color of electrolytes changes explicitly with the SOC variation and thus the spectrophotometric can be used to detect the change. Following that, the two half-cell solution potentials were further calibrated for SOC monitoring by Corcuera and Skyllas-Kazacos [75]. These methods monitor the SOC of each half-cell and aim at detecting any imbalance between the two individual half-cell electrolytes that would lead to capacity loss.

D. Model Based Estimation

The idea of model based SOC estimators is to connect the onboard measureable signals such as current and voltage to the immeasurable SOC with a battery model which is mostly in the form of state-space model. By continuously monitoring the model input (current) and output (voltage), the SOC as a system state can be estimated with a well-designed state observer. The common used battery models have already been reviewed in Section 2.4.2. Considering the unique advantages, only the ECM based SOC estimators will be discussed in this section.

A number of adaptive filters known from control theory have been employed to estimate the SOC in real time. Such filters detect any deviation between the modeled and measured terminal voltages and use it to correct the system SOC in a close-loop feedback way. The Kalman filter (KF) as the most widely used adaptive filtering technique was used on the battery since 1986. The KF is only adoptable with linear models, while the modern extensions of KF permit the use of nonlinear battery models which better reproduce the battery behaviors. The EKF has been widely used for battery SOC estimation [43, 68]. The EKF is based on the linearization of the nonlinear battery model, which will incorporate large approximation errors. To improve the linearization accuracy, the sigma-point KF (SPKF) [76-78], unscented KF (UKF) [79-81], and central difference KF (CDKF) [82] can be employed.

The KF and all its variants require knowing the covariance of the process noise and measurement noise. Incorrectness of this information may cause either poor convergence or excessively slow adaption. The adaptive EKF (AEKF) [56, 58, 83] and the adaptive UKF (AUKF) [84-86] are able to online estimate the noise covariance thus perform better than the EKF, but the computational complexity is improved quite a lot. The H-infinity filter was also employed for the merit of requiring no assumptions on the process and measurement uncertainties [51, 87]. The EKF also assumes the process and measurement noises to be Gaussian. This assumption, however, deviates from the truth in real applications. To address this problem, the particle filter (PF) [45-47] and the unscented particle filter (UPF) [88, 89] were introduced and reported to improve the accuracy of the SOC estimate. The drawback is that such methods have quite high requirements on the computational sources (by factor 50 compared to the UKF) and memory consumptions [90].

There exist lots of other types of adaptive filters for SOC estimation, for example the sliding mode observer (SMO) [91], the nonlinear predictive filter (NPF) [49], PI observer [92], and some other extensions [48, 50, 51]. The ECM based estimators have proved to be accurate and robust for battery SOC estimation. Nevertheless, it should be noted that the precondition is a well-parameterized battery model. It is proved that the ECM based SOC estimators decline significantly in accuracy if the model parameters are not appropriately defined [93]. To date, the model parameters are mostly prescribed offline with the fitting methods and left unchanged during the entire SOC estimate. In the limited literatures where the model parameters are updated online, the dual EKF (DEKF) [94, 95] or joint EKF (JEKF) [96] are usually used. As an important contribution of this thesis, the detailed literature review of online model parameters identification will not be drawn here; instead, this issue will be extensively reviewed in the introductions of the following chapters.

The least squares (LS) based filters are another category of SOC estimators. In refs. [57, 97, 98], the RLS method was employed to couple the model parameters and OCV into one vector for joint estimation, following which the SOC is referred with the SOC-OCV table. Different from the KF based filters, the RLS treats the input signals as deterministic thus the stochastic calculations are not included. The RLS

method is free from the complex matrix operations such as matrix inversion thus is easier to be used with low demand on computational resources. It also permits the update of model parameters to adapt to the change of operating condition and battery degradation. As discussed in ref. [83], however, the mapping from OCV to SOC is an open-loop way thus the accuracy is limited, especially if the battery chemistry exhibits a flat SOC-OCV curve. In addition, this method tends to suffer from divergence especially when the battery model is not accurate enough [90]. The moving window LS filter can effectively enhance the stability but requires a higher demand on computing power and memory consumption.

E. Computational Intelligence Based Method

In Section 2.4.2 B, we have shown that the computational intelligence based methods can be used in the battery model to predict the battery terminal voltage. Actually, such methods can work in the similar way but directly estimate battery SOC instead. The ANN was employed to model the relationship between SOC and the onboard measured battery signals including load current, terminal voltage and operating temperature [99-103]. Such methods demand no exact knowledge of the chemical reactions and dynamics. The obvious drawback is that the model training needs an extensive amount of data. In addition, the ANN model trained with a specific batch of data will gradually lose effectiveness as the battery characteristics change with battery aging. Similar with the ANN based direct SOC estimation, the SVM technique was also implemented in the same manner [104-107]. The SVM based direct estimation methods bear the same advantages and disadvantages as the ANN.

The close-loop SOC estimators with the ANN were reported in refs. [35, 36, 108]. An ANN based extreme learning machine (ELM) was applied in combination with the EKF in ref. [109]. The current, temperature and estimated SOC are used as the model inputs of ANN and the terminal voltage is treated as the model output. Any deviation between the model output and measured output is used to correct the SOC in a close-loop framework. Such methods is superior to the direct estimation as the online training of the model is theoretically permitted, although quite computational heavy. Compared with the ECM based estimators, such estimators are more

appropriate to be used in the condition that the battery dynamics cannot be reproduced with the simple electrical model.

2.4.4 Capacity Estimation

The capacity is a figure of merit describing the total charge (rated in ampere-hours) stored in the battery that can be used by the users when the battery is fully charged. It is also an important indicator for the SOH of the battery. For all the battery chemistries, the capacity can be viewed as an indicator of the SOH which is essential to judge the aging state of the battery.

The aging of VRB is reflected by the substantial capacity decay that occurs during cycling, which is critically important to the long-term operations. The capacity fading is basically caused by two electrochemical processes.

The imbalance of vanadium active species will occur as the cycling proceeds and results in the decay of VRB capacity. In real charge-discharge cycling, the transfer rates of V^{2+} and V^{3+} are large than those of VO^{2+} and VO_2^+ , and this will cause the net transfer of vanadium species from the negative to the positive half-cell [110]. It has also been reported that the transfer behavior of water across the exchange membrane and that of vanadium species are similar [111]. For this reason, the volume and total vanadium species concentration increase on the positive side and decrease on the negative side in cycling process. The imbalance causes the negative side to be the “limiting electrolyte” as the decreased volume and active species in negative side are not enough to consume the vanadium species in the positive side. This will give rise to the decreased utilization ratio of the vanadium species in the positive half-cell during cycling.

Apart from diffusion effects, gassing side reactions occur at both half-cells and cause fading of capacity especially during the charging process [13]. One of the side reactions that lead to capacity decay is the air oxidation of bivalent vanadium ion in the negative half-cell. This side effect will also cause the imbalance of active species in the two half-cells. Another side reaction leading to the high loss of capacity is the hydrogen evolution during charging. This effect lowers the

conversion of vanadium ions at negative electrode surface particularly at high states-of-charge and with large currents. Generally speaking, the oxygen evolution at the positive electrode has been shown to be negligible up to relatively high SOC. However, the hydrogen evolution at the negative half-cell is much more significant above 90% SOC. As a result, the VRB is usually operated between 10% and 90% SOC to prevent the aforementioned gassing side reactions and to elongate the battery calendar life.

All the above mentioned two factors exist in the VRB systems and cause imbalance among the vanadium species of different states of oxidation, thereby leading to a deteriorative capacity performance, and equivalently battery aging, during long term use.

It should be noted that the timely capacity adaption further facilitates the SOC estimation as the capacity is involved in the state equation of most ECM-based SOC observers. Despite the importance, the instantaneous capacity, analogous to the SOC, is an inner state that cannot be measured by any available sensors. Consequently, a reliable capacity estimator is highly urgent to be investigated and integrated to the BMS. The existing capacity estimation methods boil down to four groups according to the work of Waag et al. [90]

A. Voltage Measurement

In these methods [112-114], the battery OCV is measured before and after charging or discharging. The SOC can be inferred with the SOC-OCV function and further the capacity is easily estimated based on the change of SOC. The real application of such methods, however, lacks flexibility considering two obvious constraints. Firstly, the capacity update should be achieved by measuring two very different SOC levels. Secondly, a long relaxation time is required to release the overvoltage and obtain the real OCV.

The methods from ref. [115] estimated the OCV change by measuring the terminal voltage under load. The capacity can be updated when the battery is sufficiently charged or discharged. However, a reliable estimator that can accurately estimate

the OCV from the onboard measured terminal voltage is still under investigation.

B. ECM Based Estimator

The capacity can be online estimated with a well-designed ECM based estimator. The battery capacity is included into the battery model as a model parameter which is estimated by allowing the modeled terminal voltage to approach the real measured value to the largest extent. These online estimators are commonly achieved by two different approaches. The first approach lumps the model parameters and the states of interests into one vector for joint estimation. The filtering technologies including the EKF [116, 117], the UKF [118], and the RLS [119] was employed in the open literatures. These methods are easily implemented with only onboard measured current and voltage as inputs and outputs. However, the calculation is quite computational heavy with high dimension matrix operations including inversions. The high filtering order can also lead to poor numerical stability.

Another approach besides the joint estimation is the so-call dual estimation. The two approaches are fundamentally similar, i.e. applying the battery model to reproduce the battery behaviors and adaptive filters to online estimate the model parameters and essential states. However, the dual estimation methods employ two filters in parallel: one for state estimate and another for the estimation of model parameters including the capacity. Lee et al. [120] estimated the SOC and capacity dually with the DEKF. A simplified DEKF was proposed in ref. [39]. The capacity is no longer treated as a model parameter; instead, a simple ampere-hour based model which uses SOC as input is adopted. Hua et al. [121] introduced a dual nonlinear predictive filter (DNPF) for co-estimation. In refs [94, 95], the capacity was treated as a model parameter, then the full set of model parameters and SOC were estimated concurrently with the DEKF. The adaption of all relevant model parameters enhances the robustness of these methods to the operating condition variation and battery degradation. The dual SPKF (DSPEK) was employed in ref. [76] as a variant of DEKF. In ref. [122], The dual-mode sliding observer in ref. [122] and the PF in ref. [123] were employed to estimate both the SOC and the instantaneous capacity. The dual estimation demands a lower computing power than

the joint estimation. While two filters are needed, each of them has a much lower dimension thus the computational complexity brought by matrix operation is released to some extent. It has to be admitted, however, the dual estimation method is still high in computing burden which prohibits the implementation in low-cost micro-controllers.

2.4.5 Peak Power Estimation

Before the peak power is discussed, we first define the concept of Safe Operating Area (SOA). The SOA of battery is defined as the operating conditions over which the battery can be expected to operate without self-damage. The typical situations for deviating from the SOA include over-current, over-voltage, under-voltage, over-temperature, and under-temperature.

The peak power is another essential state defined as the maximum power that is possible to be accepted or delivered by the battery for the future prediction time horizon without violating the SOA. The reliable estimate of peak power enables the system to fully exploit the potential of the battery within the safe operation window. In real operation, the peak power is constrained by the design limits of current and voltage, SOC, and the temperature limit. Consequently, it changes quite a lot during routine operation and also the process of battery aging.

The dynamic battery model based online peak power estimation is a quite promising approach that can give high fidelity and robustness. A widely used method for peak power determination is the hybrid pulse power characterization (HPPC) method by the Partnership for New Generation Vehicles (PNGV) [124], which is simplified as HPPC method here. The HPPC method describes the battery dynamics with the following characterization equation:

$$V_{t,k} = V_{oc}(s_k) - I_{L,k} R_s \quad (2.4)$$

where the load current I_L is defined as positive for discharge and negative for charge. The design limit for terminal voltage should be enhanced with $V_{t,k} \in [V_{\min} \quad V_{\max}]$. Accordingly, the maximum discharge current as constrained by

voltage limitation can be derived as:

$$I_{\max,k}^{dis,volt} = \frac{V_{oc}(s_k) - V_{\min}}{R_s} \quad (2.5)$$

The maximum charge current can be determined in the same manner. Since the charge current is negative, the maximum magnitude is actually a minimum in the signed sense, which can be expressed as:

$$I_{\min,k}^{chg,volt} = \frac{V_{oc}(s_k) - V_{\max}}{R_s} \quad (2.6)$$

The peak power for a single battery can then be defined as:

$$\begin{cases} P_{\max}^{dis} = V_{\min} I_{\max,k}^{dis,volt} \\ P_{\max}^{chg} = V_{\max} I_{\min,k}^{chg,volt} \end{cases} \quad (2.7)$$

The HPPC method uses very simple battery model thus its implementation is quite easy. Zhang et al. [125] utilized the HPPC method to study the temperature dependency of power capability and an operating map of power capability. However, only the voltage constraint is considered in the HPPC method, while the other constraints on maximum current, maximum power and SOC are overlooked. In addition, the battery model is so primitive that it may cause overly optimistic or pessimistic estimations which are quite dangerous for the battery utilization. Lastly, this method estimates the instantaneous peak power. If considering the peak power for a certain time period in the future, this method will lose its effectiveness.

Plett proposed an improved peak power estimator based on the HPPC method. The limit of SOC is added to the formulation of power calculation. The SOC change under current excitation is expressed as:

$$s(t+\Delta t) = s(t) - \frac{\eta I_L \Delta t}{Q} \quad (2.8)$$

The limit for SOC should be enhanced with $s(t) \in [s_{\min} \ s_{\max}]$. Accordingly, the

maximum discharge current as constrained by SOC limitation can be derived as:

$$\begin{cases} I_{\max,k}^{dis,soc} = \frac{Q[s(t) - s_{\min}]}{\eta\Delta t} \\ I_{\min,k}^{chg,soc} = \frac{Q[s(t) - s_{\max}]}{\eta\Delta t} \end{cases} \quad (2.9)$$

Further, the calculation explicitly includes a specific time horizon which is more useful in real applications. The OCV evolvment for the next time horizon is derived to allow accurate calculation of the maximum current. The major shortcoming associated with this method is that the model is still too simplistic without polarization effects taken into account. In addition, a reliable SOC estimator which is required for this method is not addressed.

He et al. improved Plett's method by using the electrochemical-polarization (EP) model [126] and the first-order RC model [127] to consider the polarization effects. The model parameters are determined offline and the SOC is assumed to be available. Xiong et al. [128] made further improvements by integrating the AEKF based SOC estimator into the peak power calculation. As another advantage, this method can efficiently estimate the peak power capability for the next multiple sampling intervals instead of just for the next sampling interval. The online adaption of model parameters, however, is still not considered. Following their work in ref. [128], Xiong et al. [129, 130] further incorporated the RLS based online model parameters identification into the algorithm to make it better adapt to the change of operating condition and battery degradation. Pei et al. [131] used DEKF to estimate the model parameters and the SOC concurrently, based on which the peak power was estimated. The estimation results were compared with the reference values acquired from a set of well-designed experiments. Wang et al. [132] applied the direct differential algorithm to online update the model parameters of an electrical circuit model and further estimated the peak power by considering the limitation on terminal voltage. Wang et al. [133] linearized the RC network based ECMs based on the original Dynamic Matrix Control algorithm. It is shown the terminal voltage can be accurately predicted thus the method can be used for

online peak power estimation.

Efforts have also been made to improve the traditional ECMs in seeking to obtain more accurate estimate of peak power. Wang et al. [134] incorporated a nonlinear diffusion resistance, whose value is proportional to the square root of time, to overcome the potential uncertainty of the RC network based ECMs concerning long timescale prediction. Waag et al [135] proposed an improved first-order RC model that includes current dependency of the polarization resistance. Based on the battery model, the peak power was online predicted considering the voltage limitation. Feng et al. [136] proposed a state of power (SOP) estimator based on a novel ECM by adding a moving average noise to the first-order RC model. The model parameters were online updated with the recursive extended least squares (RELS) algorithm.

2.5 Summary

In this chapter, the fundamentals of the flow battery and VRB are systematically reviewed. The emphasis is placed on the related topics of the battery modeling and the model-based online estimation of key battery states, including the SOC, capacity, and peak power. Existing works have provided valuable insights into these topics. However, more works can be done to make further improvements, especially for incorporating the online model adaption, improving the estimation accuracy and robustness, and lowering down the computational complexity. Moreover, the effect of noise contamination on the accuracy of modeling and state estimation has not been adequately investigated. Driven by the high demand on battery management and control, this thesis aims to estimate the key battery states in real time with reliable algorithms which have high accuracy, high adaptivity, quick convergence, low computational burden, and high robustness to noise interference.

CHAPTER 3 An Adaptive Battery Model for Vanadium Redox Flow Battery and Its Application for Online Peak Power Estimation

3.1 Introduction

The peak power is an essential state defined as the maximum power that is possible to be accepted or delivered by the battery for the future prediction time horizon without violating the SOA. As discussed in Section 2.4.5, the reliable estimate of peak power enables the system to fully exploit the potential of VRB within the safe operation window. Despite the importance, the study on the reliable peak power estimation method for VRB is quite limited. The model based online peak power estimation is a promising approach that can give high fidelity and robustness. Yu et al. [137] developed a physics-based model to calculate the steady-state peak power. The method is essential for predicting the power range of VRB to facilitate the design optimization process. However, the simulation based theoretical analysis lacks verification for both the modeling accuracy and power estimation accuracy. The HPPC method by the PNGV [124] is more practical in real applications thus has been widely used for the lithium-ion battery. Considering the similarity in voltage response among different battery chemistries, this method can be easily extended to be used on VRB. The HPPC method uses a very simple battery model thus its implementation is quite easy. Zhang et al. [125] utilized the HPPC method to study the temperature dependency of peak power and further proposed an operating map to determine the peak power. However, the HPPC method only considers the constraint of voltage, while the other constraints on SOC and design current limit are overlooked. The battery model is also primitive so that may cause overly optimistic or pessimistic estimations which are quite dangerous for the VRB utilization. Moreover, the HPPC method estimates the instantaneous peak power, i.e. the allowable power for the present moment. If considering the peak power that can be maintained for a certain period in the future, which is quite important for the power management of the battery system, this method will lose effectiveness. In

recent years, some revised methods were studied to improve the HPPC method [125-136] as reviewed in 2.4.5. All these methods depend critically on an accurate battery model which has to be extensively investigated for VRB.

As reviewed in Section 2.4.2 A, most of the existing models for VRB are electrochemical models [25-31] which are based on complicated PDEs and thus are not realistic for real-time applications. Tang et al. [13, 138, 139] investigated several mathematical models to take the ion diffusion, side reactions, shunt current, and pressure losses into account. These mathematical models simplified the electrochemical models by using assumptions and considering only the important physical and chemical processes. The simplification remarkably reduces the computational complexity and allows online implementation. One possible drawback is that some model parameters that significantly affect the modeling results are mostly empirical and depend largely on the knowledge of inner dynamic processes. Amongst others, the ECM shows the merits of excellent adaptability, easy realization, and reasonable accuracy, thus is a favorable template for online applications.

Till now, only a few publications can be found concerning ECMs applied to the VRB. Chahwan et al. [60] proposed a simple ECM to obtain the energy content and terminal voltage profile of VRB, aiming to study the applications in power systems. The proposed simple ECM was used for the stand-alone wind energy system simulation and grid-connected wind farm power control [61-63]. Qiu et al. [15] further simplified the model and utilized it for controller design of a microgrid with photovoltaic. Later, the simple model was extended to incorporate the environmental controls by the heating, ventilation, and air conditioning system to provide a more realistic efficiency profile [64]. The simple ECM and its variants introduce the system losses such as pump loss and parasitic loss which are quite insightful for the VRB study; however, they are aimed for system simulation where the requirement on modeling accuracy is not high. The losses are also estimated empirically without detailed explanations. Moreover, the models have not been verified with real experimental data. In recent years, multiple ECMs for VRB with new structures have been reported. Wei et al. [66-68] integrated the thermal model

into the ECM to ensure the model fidelity over a wide range of operating conditions. Zhang et al. discussed a comprehensive ECM by taking the transient process, shunt current and vanadium iron diffusion into account [69]. One common drawback of these models is that the model parameters which are crucial for modeling accuracy are determined empirically without detailed method for identification. In order to tackle this problem, Mohamed et al. [59] proposed to use the second-order RC model for VRB and adopted the EKF to identify the model parameters. The seventh-order EKF, however, will cause extensive calculation of high-dimension matrices which is quite computational heavy. The high order filter may also be subject to instability issues.

In this chapter, the first-order RC model [140-142] is applied to simulate the dynamics of VRB. Two model identification methods, RLS and EKF, are adopted to compare their performance on tracking the time varying model parameters with a simulation study. Based on the online identified model, an online adaptive peak power estimator is proposed by considering multiple constraints including the voltage limit, SOC limit, and design current limit. Experiments are conducted on a lab-scale VRB system to verify the proposed method for model identification and a “two-step verification” method is used to evaluate the accuracy of the proposed peak power estimator. After that, the peak power estimation for a hybrid pulse experiment is illustrated and the influence of prediction time horizon on estimation result is analyzed.

The rest of the chapter is organized as follows. Section 3.2 introduces the applied battery model and compares two online identification methods, RLS and EKF, on their identification accuracy, convergence property and computational complexity with a simulation study. Section 3.3 discusses the proposed model-based peak power estimator based on the online identified battery model. Section 3.4 describes the experimental setup and procedures for performance evaluation. Section 3.5 presents the algorithm verification and discussion, while Section 3.6 draws the key conclusions.

3.2 Battery Model

3.2.1 Battery Modeling

The behavior of VRB is highly nonlinear thus a reliable battery model is paramount. The ECM which has high adaptability, low complexity, and reasonable accuracy is of interest throughout this thesis. The choice of ECM is always a trade-off between modeling accuracy and computational complexity. Hu et al. [52] studied the major ECMs and concluded the first-order RC model as the best choice to manage the trade-off between complexity and accuracy. In this regard, the first-order RC model is used in this chapter. It has to be mentioned, however, that the method proposed here is applicable to a broad range of higher-order battery models.

Figure 3.1. Schematic diagram of the first-order RC model

The structure of the applied first-order RC model is shown in Figure 3.1. The voltage source represents the OCV which is measured with the open-circuit cell in real time. R_s , R_p , and C_p are the model parameters to be identified. Specifically, R_s is the ohmic resistance including component resistance and contact resistance between components, and is a dependent on temperature, SOC, and aging level. The RC network is used to simulate any transient dynamics involved in VRB. The constant phase element (CPE) and Warburg impedance term which provide more detailed description of the dynamic process is omitted in this study aiming at reducing model complexity and enhancing numerical stability. Despite the simplification, we will verify in the following sections that the used model is still high highly accurate if the model parameters are appropriately adapted.

The electrical behavior of the first-order RC model can be expressed by the following state equations:

$$C_p \frac{dV_p}{dt} + \frac{V_p}{R_p} = I_L \quad (3.1)$$

$$V_t = V_{oc} - V_p - I_L R_s \quad (3.2)$$

where I_L denotes the load current which is defined as positive for discharge and negative for charge throughout this thesis; V_{oc} denotes the OCV; V_p denotes the polarization voltage across the RC network; while V_t is the terminal voltage. Eq. (3.1) can be rewritten in the discrete-time form as:

$$V_p(t) = e^{-\frac{t_s}{R_p C_p}} V_p(t - t_s) + (1 - e^{-\frac{t_s}{R_p C_p}}) R_p I_L(t - t_s) \quad (3.3)$$

where t_s is the onboard sampling time interval of current and voltage signals.

3.2.2 Online Model Identification

The model parameters are commonly prescribed offline with the training dataset. However, they are time varying with lots of factors, such as working temperature, operating flow rate, SOC, current direction and magnitude. In addition, the model parameters are also subject to variations as the battery ages after long time cycling. Considering this, online model identification is indispensable to handle the aforementioned model uncertainties and to guarantee the modelling accuracy. For this purpose, the RLS-based and EKF-based online model identification methods are introduced in this section.

A. Recursive Least Squares

By substituting Eq. (3.2) into Eq. (3.3), the following expression can be drawn:

$$V_e(t) = \alpha_1 V_e(t - t_s) + \alpha_2 I_L(t) + \alpha_3 I_L(t - t_s) \quad (3.4)$$

where

$$V_e(t) = V_t(t) - V_{oc}(t)$$

$$\begin{bmatrix} \alpha_1 & \alpha_2 & \alpha_3 \end{bmatrix} = \begin{bmatrix} e^{-\frac{t_s}{R_p C_p}} & -R_s & R_s e^{-\frac{t_s}{R_p C_p}} - (1 - e^{-\frac{t_s}{R_p C_p}}) R_p \end{bmatrix} \quad (3.5)$$

The OCV is continuously measured with an open-circuit cell in this chapter; therefore, the value of V_e can be easily obtained at each time point. Within this context, Eq. (3.4) can be expressed in a regression form as:

$$V_e(t) = \phi^T(t)u(t) \quad (3.6)$$

where

$$\phi(t) = \begin{bmatrix} \alpha_1 & \alpha_2 & \alpha_3 \end{bmatrix}^T$$

$$u(t) = \begin{bmatrix} V_e(t-t_s) & I_L(t) & I_L(t-t_s) \end{bmatrix}^T \quad (3.7)$$

The RLS method is a computational efficient method to solve the regression model represented by Eq. (3.6). A user-defined forgetting factor λ is employed in order to emphasize the significance of the most recently obtained data and give less weight to the old data. The algorithmic procedures of RLS with forgetting (exponential weighting) are not elaborated here but can be referred to existing literatures [143]. In this chapter, a forgetting factor of 0.985 is used. After the regression model is solved, the model parameters can be reversely deducted as:

$$\begin{bmatrix} R_s & R_p & C_p \end{bmatrix} = \begin{bmatrix} -\alpha_2 & \frac{\alpha_1 \alpha_2 + \alpha_3}{\alpha_1 - 1} & \frac{(1 - \alpha_1) t_s}{(\alpha_1 \alpha_2 + \alpha_3) \ln \alpha_1} \end{bmatrix} \quad (3.8)$$

With the online extracted model parameters, the terminal voltage at the next sampling time can be easily modeled.

B. Extended Kalman Filter

The KF is a set of mathematical equations that provide an efficient recursive means for the state estimation problems. The estimation achieved by minimizing mean of the squared error is optimum for a linear system. The EKF as a nonlinear version of

the KF uses linearization at each time step to approximate the nonlinear system with a linear time varying (LTV) system. Then the same procedures of KF are applied on the LTV system. The state-space model of VRB in discrete-time domain can be written as follows:

$$\begin{aligned} x_{k+1} &= F(x_k, u_k) + w_k \\ y_k &= G(x_k, u_k) + v_k \\ w_k &\sim (0, \Sigma_w) \\ v_k &\sim (0, \Sigma_v) \end{aligned} \quad (3.9)$$

where w_k and v_k are the process noise and measurement noise, which are independent, zero-mean, and Gaussian processes with covariance matrices Σ_w and Σ_v . The theoretical details of EKF can be found in Ref [144], while the five-step procedures of EKF are summarized in Table 3.1.

Table 3.1 Algorithmic Procedure of EKF

Initialize $\hat{x}_0^+$, Σ_w and Σ_v ; For $k = 1, 2, \dots$	
Update of priori state:	$\hat{x}_k^- = F(\hat{x}_{k-1}^+, u_{k-1})$
Update of priori error covariance:	$\Sigma_{x,k}^- = \hat{A}_{k-1} \Sigma_{x,k-1}^+ \hat{A}_{k-1}^T + \Sigma_w$
Update of Kalman gain:	$L_k = \Sigma_{x,k}^- \hat{C}_k^T [\hat{C}_k \Sigma_{x,k}^- \hat{C}_k^T + \Sigma_v]^{-1}$
Update of posteriori state:	$\hat{x}_k^+ = \hat{x}_k^- + L_k [y_k - G(\hat{x}_k^-, u_k)]$
Update of Posteriori error covariance:	$\Sigma_{x,k}^+ = (I - L_k \hat{C}_k) \Sigma_{x,k}^- (I - L_k \hat{C}_k)^T + L_k \Sigma_v L_k^T$

The follows go further to generalize the characterization equations of VRB into the form of Eq. (3.9) so that the procedures listed in Table 3.1 can be implemented. For this purpose, the system state (x), system input (u), and system output (y) are firstly defined as:

$$\begin{aligned} x &= [V_p \quad 1/R_p \quad 1/C_p \quad R_s] \\ u &= I_L \\ y &= V_t \end{aligned} \quad (3.10)$$

It is assumed the model parameters vary in a low rate, so that it can be confirmed that $1/R_{p,k+1} \approx 1/R_{p,k}$, $1/C_{p,k+1} \approx 1/C_{p,k}$, and $R_{s,k+1} \approx R_{s,k}$. Transforming Eq. (3.3) into the form of Eq. (3.9) yields:

$$\begin{aligned} x_{k+1} &= F(x_k, u_k) = \begin{bmatrix} F_{1,k} & F_{2,k} & F_{3,k} & F_{4,k} \end{bmatrix}^T \\ y_k &= G(x_k, u_k) = V_{oc,k} - x_{1,k} - x_{4,k} u_k \end{aligned} \quad (3.11)$$

where F_i ($i = 1, 2, 3, 4$) can be expressed as:

$$\begin{aligned} F_1 &= \exp(-t_s x_2 x_3) x_1 + [1 - \exp(-t_s x_2 x_3)] \frac{u}{x_2}, \\ F_2 &= x_2, F_3 = x_3, F_4 = x_4 \end{aligned} \quad (3.12)$$

where x_i is the i -th element of x .

Specifically, $\hat{A}_k$ is the Jacobian matrix of partial derivatives of $F(\bullet)$ with respect to x , and can be expressed by:

$$\hat{A}_k = \frac{\partial F}{\partial x} \bigg|_{x_k = \hat{x}_k^+} = \begin{bmatrix} \frac{\partial F_1}{\partial x} \bigg|_{x_k = \hat{x}_k^+} & \frac{\partial F_2}{\partial x} \bigg|_{x_k = \hat{x}_k^+} & \frac{\partial F_3}{\partial x} \bigg|_{x_k = \hat{x}_k^+} & \frac{\partial F_4}{\partial x} \bigg|_{x_k = \hat{x}_k^+} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad (3.13)$$

where the partial derivative terms are solved as:

$$\begin{aligned} \frac{\partial F_1}{\partial x} \bigg|_{x_k = \hat{x}_k^+} &= \exp(-t_s x_2 x_3) \bigg|_{x_k = \hat{x}_k^+} \\ \frac{\partial F_2}{\partial x} \bigg|_{x_k = \hat{x}_k^+} &= -t_s x_1 x_3 \exp(-t_s x_2 x_3) - \frac{u_k}{x_2^2} + u_k \left(\frac{1}{x_2^2} + \frac{t_s x_3}{x_2} \right) \exp(-t_s x_2 x_3) \bigg|_{x_k = \hat{x}_k^+} \\ \frac{\partial F_3}{\partial x} \bigg|_{x_k = \hat{x}_k^+} &= (u_k t_s - t_s x_1 x_2) \exp(-t_s x_2 x_3) \bigg|_{x_k = \hat{x}_k^+} \\ \frac{\partial F_4}{\partial x} \bigg|_{x_k = \hat{x}_k^+} &= 0 \end{aligned} \quad (3.14)$$

Meanwhile, $\hat{C}_k$ as the partial derivative of $G(\bullet)$ with respect to x is given by:

$$\hat{C}_k = \left[\frac{\partial G}{\partial x_1} \quad \frac{\partial G}{\partial x_2} \quad \frac{\partial G}{\partial x_3} \quad \frac{\partial G}{\partial x_4} \right]_{x_k = \hat{x}_k^+} = [-1 \quad 0 \quad 0 \quad u_k] \quad (3.15)$$

With aforementioned definitions and derivations, the EKF can be applied according to Table 3.1 to identify the model parameters in real time.

C. Performance Comparison

In this section, a simulation study is carried out to compare the two identification methods on the current case. The ECM shown in Figure 3.1 is built in Matlab Simulink environment. The model parameters (R_s , R_p , C_p) are user defined so that the identification result by the two methods can be evaluated. The applied load current is shown in Figure 3.2, while the simulated terminal voltage, SOC, and OCV are shown in Figure 3.3. The system is sampled at an interval of 1 s.

Figure 3.2 Profile of load current for the simulation study

As no prior knowledge of the model parameters and system states are available before the simulation, they are randomly initialized as: $R_s = 0 \text{ m}\Omega$, $R_p = 1 \text{ m}\Omega$, $C_p = 2 \text{ kF}$, $V_p = 0 \text{ V}$. The convergence of EKF depends largely on the selection of covariance matrices, i.e. initial state covariance ($\Sigma_{x,0}$), process noise covariance (Σ_w) and measurement noise covariance (Σ_v). For the current case, they are tuned

as: $\Sigma_{x,0} = \text{diag}[10^{14} \quad 10^{14} \quad 10^{14} \quad 10^5]$, $\Sigma_w = \text{diag}[1 \quad 10^8 \quad 10^{-5} \quad 10^{-1}]$, $\Sigma_v = 10^{-5}$.

Figure 3.3 Profile of terminal voltage, SOC, and OCV for the simulation study

The identification results by the two methods are plotted in Figure 3.4, Figure 3.5, and Figure 3.6 for R_s , R_p , and C_p , respectively. As can be observed, the two algorithms both correct the erroneous initialization and converge to the true values quickly. After that, the online identified results demonstrate good agreement with the pre-defined values. It should be noted that the model parameters from the simulation study are defined based on the physical and electrochemical processes in VRB. The concentration overpotential appears when the supply of reactants at the electrode or the removal of the reaction products is rate-determining when current flows. The concentration overpotential has been reported to be high at low SOC regions. Therefore, a continuously increased polarization resistance is used and the significant overpotential can be easily observed in the voltage response shown in Figure 3.3. In contrast, the polarization capacitor is used to represent the charge double layer on or near the electrode/electrolyte interface. The capacitance value depends majorly on the electrical permittivity, actual surface area of the electrode, and the separation of the plates [145], so it is assumed to be constant during the cycling.

Figure 3.4 Online identification result of R_s for the simulation study

Figure 3.5 Online identification result of R_p for the simulation study

Figure 3.6 Online identification result of C_p for the simulation study

In order to better evaluate the convergence property, the convergence time defined as the time after which the identification enters the 5% error bound is applied. The computational cost is an indispensable consideration for real applications, so that the CPU time for each iteration is also used as a performance measure. The comparison of the two methods on convergence time, mean absolute error (MAE), root mean square error after convergence (RMSE), and CPU time are summarized in Table 3.2. As suggested, the EKF generates a slightly higher accuracy, if observable, than the RLS after convergence. It should be noted, however, that the RLS can completely fulfill the requirement of online identification considering the sufficiently small errors. The EKF needs a significantly longer time to converge compared with the RLS. This is within our expectation as it has been reported that the high order EKF may suffer from instability conditions [42]. Even though the covariance matrices have been extensively tuned to improve the stability, the algorithm still spends more effort to converge especially at the start-up stage. The CPU time of EKF is also much higher than RLS, which is caused by two reasons. Firstly, the recursive calculation of EKF has higher computational complexity than RLS from the algorithmic perspective. Secondly, the order of EKF is higher than that of RLS and the higher-dimension matrix operation unavoidably occupies more

computing resources. Taking all the measures into consideration, we conclude that the RLS is more appropriate for VRB model identification especially when the computational resources are limited.

Table 3.2 Performance comparison of RLS and EKF on model identification for the simulation study

	RLS			EKF		
	R_s	R_p	C_p	R_s	R_p	C_p
Convergence time	60 s	179 s	183 s	72 s	301 s	306 s
MAE	0.20%	0.78%	0.68%	0.11%	0.75%	0.71%
RMSE	0.25m Ω	4.51m Ω	4.49kF	0.78m Ω	2.99m Ω	6.75kF
CPU time	46.7 μ s			73.4 μ s		

3.3 Adaptive Peak Power Estimation

Based on the online adapted battery model presented in Section 3.2, this section aims to develop an adaptive peak power estimator for VRB by considering multiple constraints.

3.3.1 Peak Current Constrained by Voltage

The first constraint should be considered is the upper and lower cut-off voltage for VRB operation. For instance, when the terminal voltage is low, the peak discharge power should be carefully controlled to avoid exceeding the lower cut-off value. The following attempts to derive the detailed calculation method of the peak current under the constraint of voltage.

The load current is assumed to be constant between the k -th sampling time t_k and the $(k + L)$ -th sampling time t_{k+L} , where L represents the prediction time horizon. Under the excitation of the peak discharge current, the terminal voltage drops to the lower cut-off voltage ($V_{t,min}$) from time t_k to t_{k+L} , so that the following equation can be drawn:

$$V_{t,\min} = V_{oc}(k+L) - V_p(k+L) - I_{L,\max}^{dis,volt} R_s \quad (3.16)$$

where $I_{L,\max}^{dis,volt}$ is the peak discharge current constrained by voltage. The polarization voltage at the $(k+L)$ -th sampling time can be expressed with the battery model as:

$$V_p(k+L) = e^{-\frac{Lt_s}{R_p C_p}} V_p(k) + (1 - e^{-\frac{t_s}{R_p C_p}}) R_p \sum_{j=1}^L e^{-\frac{(j-1)t_s}{R_p C_p}} I_{L,\max}^{dis,volt} \quad (3.17)$$

In order to derive $V_{oc}(k+L)$, the SOC recurrent relationship is firstly introduced as:

$$s(k+L) = s(k) - \frac{\eta I_{L,\max}^{dis,volt} Lt_s}{Q} \quad (3.18)$$

Then the Taylor series approximation of V_{oc} around $s(k)$ is written as:

$$\begin{aligned} V_{oc}(k+L) &= V_{oc} \left[s(k) - \frac{\eta I_{L,\max}^{dis,volt} Lt_s}{Q} \right] \\ &= V_{oc}(k) - \frac{\eta I_{L,\max}^{dis,volt} Lt_s}{Q} \left. \frac{dV_{oc}}{ds} \right|_{s(k)} + r \left[s(k), \frac{\eta I_{L,\max}^{dis,volt} Lt_s}{Q} \right] \end{aligned} \quad (3.19)$$

where $r(\bullet)$ is the remainder term of Taylor approximation which is quite small thus can be ignored.

By integrating Eq. (3.16), (3.17), and (3.19), the final expression of the voltage-constrained peak discharge current is:

$$I_{L,\max}^{dis,volt}(k) = \frac{V_{oc}(k) - e^{-\frac{Lt_s}{R_p C_p}} V_p(k) - V_{t,\min}}{\frac{\eta Lt_s}{Q} \left. \frac{dV_{oc}}{ds} \right|_{s(k)} + (1 - e^{-\frac{t_s}{R_p C_p}}) R_p \sum_{j=1}^L e^{-\frac{(j-1)t_s}{R_p C_p}} + R_s} \quad (3.20)$$

As all the model parameters (R_s , R_p , C_p) have been updated in real time, and OCV and SOC are measured with the open-circuit cell, it is explicit that Eq. (3.20) can be solved.

The voltage-constrained peak charge current can be determined in the same manner. Since the charge current is negative, the maximum magnitude is actually a minimum in the signed sense, so we define the peak charge current as $I_{L,\min}^{chg,volt}$, which can be expressed as:

$$I_{L,\min}^{chg,volt}(k) = \frac{V_{oc}(k) - e^{-\frac{Lt_s}{R_p C_p}} V_p(k) - V_{t,\max}}{\frac{\eta Lt_s}{Q} \frac{dV_{oc}}{ds} \Big|_{s(k)} + (1 - e^{-\frac{t_s}{R_p C_p}}) R_p \sum_{j=1}^L e^{-\frac{(j-1)t_s}{R_p C_p}} + R_s} \quad (3.21)$$

where $V_{t,\max}$ is the upper cut-off voltage of VRB.

3.3.2 Peak Current Constraint by SOC

The SOC has to be maintained within a certain range to improve the efficiency and elongate the life calendar. For instance, too large discharge current for a certain time horizon will cause over-discharge when the SOC is close to the lower design constraint. To this end, the allowed peak discharge current should be controlled to protect the battery.

While the VRB is reported to have relatively high tolerance to over-charge and over-discharge, they should still be avoided in real applications. The severe over-discharge will cause cell reversal which is detrimental for battery performance. The effect of over-charge is much more complicated. Firstly, gassing side reactions will occur at both half-cells and cause fading of capacity especially during the charging process [13]. Although the oxygen evolution at the positive electrode has been shown to be negligible up to relatively high SOC, the hydrogen evolution at the negative half-cell is much more significant above 90% SOC. Gas evolution can also interrupt the electrolyte flow and lead to the changes of pH. Moreover, severe over-charge conditions can lead to the oxidation of the carbon black materials used in the bipolar electrode substrate which further causes the increase of resistance. The oxidation of graphite felt materials will form the carbon/oxygen functional groups which are removable under reducing conditions. However, the oxidation of the

more reactive carbon black filler material can lead to CO₂ formation resulting in delamination and destruction of the composite matrix. As a result, the VRB is recommended to be operated within a certain SOC region to prevent the aforementioned issues and to elongate the battery calendar life.

In this section, it is assumed the limit for SOC should be enhanced with $s \in [s_{\min} \quad s_{\max}]$. Accordingly, the peak discharge and charge current constrained by SOC limit can be derived from Eq. (3.18) as:

$$\begin{cases} I_{L,\max}^{dis,soc}(k) = \frac{Q[s(k) - s_{\min}]}{\eta L t_s} \\ I_{L,\min}^{chg,soc}(k) = \frac{Q[s(k) - s_{\max}]}{\eta L t_s} \end{cases} \quad (3.22)$$

3.3.3 Peak Power Calculation

Once the peak currents constrained by the voltage and SOC are obtained, the peak current under all constraints can be calculated as:

$$\begin{cases} I_{L,\max}^{dis}(k) = \min[I_{L,\max}^{dis,vol}(k), I_{L,\max}^{dis,soc}(k), I_{L,\max}] \\ I_{L,\min}^{chg}(k) = \max[I_{L,\min}^{chg,vol}(k), I_{L,\min}^{chg,soc}(k), I_{L,\min}] \end{cases} \quad (3.23)$$

where $I_{L,\max}$ and $I_{L,\min}$ are the design limits of discharge and charge current, respectively. After the peak current is determined, the discharge voltage and charge voltage during the prediction time horizon can be derived as Eq. (3.24) and Eq. (3.25), respectively.

$$\begin{aligned} V_t(k+i) = V_{oc}(k) - e^{-\frac{it_s}{R_p C_p}} V_p(k) \\ - \left[\frac{\eta i t_s}{Q} \frac{dV_{oc}}{ds} \right]_{s(k)} + (1 - e^{-\frac{t_s}{R_p C_p}}) R_p \sum_{j=1}^i e^{-\frac{(j-1)t_s}{R_p C_p}} + R_s \Big] I_{L,\max}^{dis}(k) \end{aligned} \quad (3.24)$$

$$V_t(k+i) = V_{oc}(k) - e^{-\frac{it_s}{R_p C_p}} V_p(k) - \left[\frac{\eta i t_s}{Q} \frac{dV_{oc}}{ds} \right]_{s(k)} + (1 - e^{-\frac{t_s}{R_p C_p}}) R_p \sum_{j=1}^i e^{-\frac{(j-1)t_s}{R_p C_p}} + R_s \Big] I_{L,\min}^{chg}(k) \quad (3.25)$$

Based on the above derivations, the power sequence under the peak current for the whole prediction time horizon can be expressed as:

$$\begin{cases} P_{dis}(k+i) = I_{L,\max}^{dis}(k) V_t(k+i) \\ P_{chg}(k+i) = I_{L,\min}^{chg}(k) V_t(k+i) \end{cases} \quad (3.26)$$

where $i = 1, 2, \dots, L$

By choosing the power values closest to zero, i.e. the minimum discharge power and the maximum charge power, the final expression of peak power by considering all the constraints can be drawn as:

$$\begin{cases} P_{peak}^{dis}(k) = \min_{i=1,2,\dots,L} [P_{dis}(k+i)] \\ P_{peak}^{chg}(k) = \max_{i=1,2,\dots,L} [P_{chg}(k+i)] \end{cases} \quad (3.27)$$

3.4 Experiment Design

3.4.1 Experimental Setup

The schematic of the experimental setup is shown in Figure 3.7. A 100 cm² (10 cm×10 cm) single VRB cell was utilized in the experiment. 80 mL of vanadium electrolyte (comprising 1.6 M vanadium in 4.5 M total sulfate) was placed in each electrolyte reservoir. The anion type membrane (FAP450) was use to separate the half cells, while the graphite felt (GFD 4.6EA from SGL Carbon) was used as the electrode material. A battery cycler NEWARE BTS-3000 was used to load the current or profiles on the battery under test. The range of current and voltage of the battery cycler are 10 A and 5 V, while the measurement error limits of sensors inside are within 0.1%. The host computer was used for current profiles editing and measurement data storage. Meanwhile, another cell (the open-circuit cell) with area

20 cm² was physically connected to the electrolyte feed pipes at the inlet of the test cell to record the battery OCV in real time. This cell was connected to another channel of the battery cycler but no current was applied, allowing the battery OCV to be continuously measured. Once the OCV was measured, the SOC could be inferred from the SOC-OCV look-up table which will be discussed in Section 3.4.2. The ambient temperature was monitored to be stable at 22±1°C throughout the tests. The flow rate was controlled with two peristaltic pumps. The flow rate was controlled at 120 mL min⁻¹ with two peristaltic pumps.

Figure 3.7 Schematic of experimental setup

3.4.2 SOC-OCV Look-up Table

Traditionally, the Nernst equation is applied but discrepancy exists between modeling and true experimental data [146]. As discussed by Corcuera and Skyllas-Kazacos [75], this discrepancy is associated with variations in hydrogen ion concentration and errors in estimation of the activity coefficients of the ions in the highly concentrated electrolyte. Throughout this thesis, therefore, the SOC-OCV curve was determined experimentally under present temperature conditions and electrolyte composition. The detailed testing procedures are described as follows.

The cell is firstly charged with constant current- constant voltage (CCCV) mode. Specifically, the cell is charged with 4 A up to the upper voltage limit of 1.65 V and then charged under constant 1.65 V to the lower cut-off current of 1 A. The OCV is

then measured for the initial state with the open-circuit cell. Then the fully charged cell is discharged by 18 segments of current pulses to the lower cut-off voltage of 0.9 V. The cell SOC is recorded with the CC method with the compensation of coulombic efficiency. At the end of each discharging segment, the OCV is measured for each SOC point to characterize the SOC-OCV relationship for discharging process. Similarly, the fully discharged cell is then charged with current pulses to acquire the SOC-OCV correlation for charging process. The final SOC-OCV curve is averaged from the data of charge and discharge process. In this way, the look-up table from SOC to OCV can be experimentally determined.

3.4.3 Hybrid Pulse Experiment for Model Verification

The hybrid pulse experiment is carried out to verify the proposed ECM in modeling battery dynamics, and the feasibility of the model identification method. The current shown in Figure 3.8 is loaded on the VRB under test as input, and the terminal voltage responses are continuously recorded. The recorded terminal voltage will be used to compare with the modeled result to evaluate the model accuracy.

Figure 3.8 Current profile of the hybrid pulse experiment

The accuracy of model parameters identification is crucial to the peak power estimation. Therefore, the reference values of model parameters should be extracted to verify the result of online model identification. To achieve this, a few discretized

time points are selected during the hybrid pulse experiment at a certain time interval, and at each time point the reference model parameters are extracted offline. Specifically, a batch of current and voltage data are sampled to form a data set around each time point. At each time point, the ohmic resistance (R_s) is extracted by calculating the instantaneous voltage jump following a step change of current, i.e. $R_s = \Delta V_t / \Delta I_L$. The polarization resistance and capacitance (R_p , C_p) are obtained by the least squares-based curve fitting to match the modelled transient voltage response to the measurements.

3.4.4 Experiment for Peak Power Verification

In this section, an experiment is designed to verify the proposed peak power estimator. The proposed peak power estimator is based on the calculation of peak current by Eq. (3.23), and the prediction of power sequence within the prediction horizon by Eq. (3.26); therefore, both the two equations have to be verified. In Eq. (3.23), the calculation of $I_{L,\max}^{dis,soc}$ and $I_{L,\min}^{chg,soc}$ with Eq. (3.22) is based on the definition of SOC, thus can be viewed as a standard method and needs no further verification. Meanwhile, $I_{L,\max}$ and $I_{L,\min}$ are the design limits of discharge and charge current which depend on the specific battery chemistries and no verification is need. In this regard, the verification of Eq. (3.23) is equivalent to verifying the voltage-constrained peak current as calculated in Eq. (3.20) and Eq. (3.21). According to the aforementioned analysis, the verification of the proposed peak power estimator boils down to verify the calculation of Eq. (3.20), Eq. (3.21), and Eq. (3.26). By selecting the prediction time horizon as 20 s, the verification experiment is described as follows.

Step 1: The VRB is firstly charged sufficiently, after which the current as shown in Figure 3.8 is loaded on the test VRB.

Step 2: The regular hybrid pulse experiment is interrupted at 1000 s, following which a large discharge current pulse of 8 A is injected to the VRB to test the voltage response. The terminal voltages during the first 20 s of the large pulse are defined as V_{20s}^{dis} . The recorded current and voltage data during the 8 A pulse will be

used to verify the estimate of the peak discharge power. The same process is repeated but interrupted at 5000 s and 9000 s for further verification.

Step 3: The regular hybrid pulse experiment is interrupted at 3000 s, following which a large charge current pulse of 8 A is injected to the VRB to test the voltage response. The terminal voltages during the first 20 s of the large pulse are recorded and defined as V_{20s}^{chg} . This process is repeated but interrupted at 7000 s to verify the estimate of the peak charge power.

According to the aforementioned steps, there will be five experiments to be carried out, three for the verification of peak discharge power estimation and two for the verification of peak charge power estimation. For each experiment, the following “two-step verification” should be conducted (taking the peak discharge power as example):

Firstly, the peak discharge current calculated by Eq. (3.20) should be verified. The last value of V_{20s}^{dis} is assumed to be the lower cut-off voltage in this case. Under this assumption, a situation is formulated that the VRB reaches the lower cut-off voltage within 20 s under the 8 A discharge current, and it is evident that the true voltage-constrained peak current is equal to 8 A. Therefore, the peak current calculation is verified if the output of Eq. (3.20) is also 8 A.

Secondly, the power sequence within the prediction time horizon under the assumed peak current (8A) should be verified. As the voltage response under the 8 A pulse has been measured in the designed experiment, the reference power sequences for the prediction horizon can be easily obtained experimentally. Then the real-time power estimation can be verified if the estimated values by Eq. (3.26) are benchmarked with the reference values.

The proposed peak power estimator is verified if the “two-step verification” is achieved. The verification of the peak charge power estimation can be conducted in the same manner.

3.5 Verification and Discussion

3.5.1 Model Verification

The accuracy of the model parameters is crucial for the peak power prediction. In this section, the RLS based real-time model identification method is applied to the current and voltage data from the hybrid pulse experiment described in Section 3.4.3 for verification purpose. As no prior knowledge is available about the model parameters, they are randomly initialized as $R_s = 0 \text{ m}\Omega$, $R_p = 1 \text{ m}\Omega$, $C_p = 2 \text{ kF}$.

Figure 3.9 Result of online model identification for the hybrid pulse experiment

The online identified model parameters along with the reference values of them are plotted in Figure 3.9. It is obvious that the model parameters are time variant thus using offline-extracted and constant values is not preferable. By adopting the proposed method, it is observed that the model parameter identification converges quickly from the erroneous initialization and the identified results are very close to the reference values. Due to the mechanism of online adaption, the frequent calibration of battery model can be avoided.

Figure 3.10 Modeling result of terminal voltage and modeling error for the hybrid pulse experiment

To further verify the accuracy of the adaptive ECM, the modeled terminal voltage with the online identified model parameters is compared with the measured data, as shown in Figure 3.10. The result suggests that the modeled voltage tracks the experimental profile with high accuracy. The modeling error is constrained within 2 mV error bound for most of the time excluding several error spikes. The high modeling accuracy reconfirms the fidelity of the applied ECM and the associated model identification method, which is the prerequisite of accurate peak power

estimate. The proposed method also proves to be robust to the initialization uncertainties.

3.5.2 Verification of Peak Power Estimation

After determining the real-time model parameters and the adaptive battery model, the proposed peak power estimator will be verified in this section. As discussed in Section 3.4.4, the verification consists of two steps, i.e. verifying the calculation of peak current and verifying the power sequence within the prediction time horizon under the assumed peak current, which will be discussed respectively as follows.

A. Verification of Voltage-constrained Peak Current Calculation

This part corresponds to the first step of the “two-step verification” discussed in Section 3.4.4. The peak current estimation result for the selected five time points is plotted in Figure 3.11. It is observed that the estimated peak currents demonstrate good agreement with the true values for all the five selected time points. The MRE of estimation is 2.36%. The best estimation occurs at 9000 s and the relative error of estimation is only 0.21%. In contrast, the worst result occurs at 7000s and the relative error of estimation is 4.62%. To give insights into the different estimation errors, the details of current in regular cycling as well as the current pulse interruption at different time points are shown in Table 3.3. It is observed that the estimation error is generally in positive correlation with the extent of current change in both direction and magnitude. At 7000 s, the regular cycling is undergoing a discharge current of 2A, which is interrupted by a large charge current of -8 A. The sudden and drastic change of current in both direction and magnitude causes a non-ignorable variation of the model parameters. However, as a prediction issue in real applications, the proposed method has to use the model parameters identified at 7000 s for the future 20 s without update. Therefore, the relatively large estimation error is within expectation. It has to be noted, however, that the relative error of 4.62% is quite acceptable for online estimation, especially when it represents the worst situation.

Figure 3.11 Peak current estimation result and estimation error

Table 3.3 Details of current in regular cycling and current pulse interruption

	1000 s	3000 s	5000 s	7000 s	9000 s
Regular current	2 A	-0.8 A	0 A	2 A	2.4 A
Interruption current	8 A	-8 A	8 A	-8 A	8 A

B. Verification of Power Sequence Estimation under Peak Current

This part corresponds to the second step of the “two-step verification” discussed in Section 3.4.4. The estimated terminal voltage and power compared with their measured values during the whole prediction time horizon is shown in Figure 3.12. The result suggests that the proposed method can accurately project the trajectory of both terminal voltage and power with high accuracy during the prediction time horizon. The estimation error is caused by the model uncertainty, including the identification errors of model parameters, and the non-update of them for the whole prediction time horizon. For example, at the instant of 5000 s, one cannot know the current and voltage information of the next prediction time horizon; hence the model parameters cannot be updated for the future moments. Instead, we have to use the model parameters updated at 5000 s to predict the peak power for the next

prediction time horizon, i.e. 5000 s to 5020 s when a time horizon of 20 s is used. The MAE of estimation is summarized in Table 3.4. Consistent with the result of peak current estimation, the best estimation happens at 9000 s while the worst happens at 7000 s. The MAE values show sufficiently high estimation accuracy for both terminal voltage and power within the prediction time horizon, thus the verification is confirmed.

Figure 3.12 Estimation results of terminal voltage and power under defined peak current within the prediction time horizon

Table 3.4 MAE of estimation for terminal voltage and power sequence

	1000s	3000s	5000s	7000s	9000s
Terminal voltage (mV)	3.25	4.31	5.61	8.22	1.87
Real-time power (mW)	25.99	34.37	44.92	65.73	14.87

3.5.3 Voltage- and SOC-constrained Peak Power

This section goes further to demonstrate the result of online peak power estimation under the hybrid pulse experiment. The upper and lower cut-off thresholds for SOC, terminal voltage, and design current limit is summarized in Table 3.5.

Table 3.5 Upper and lower cut-off thresholds for SOC, terminal voltage, and design current limit

	Maximum	Minimum
SOC	96%	10%
V_t	1.65	1.20
I_L	8 A	-8 A

To ease the analysis, we firstly ignore the design current limit and only consider the constraints of terminal voltage and SOC. We also investigate how the prediction time horizon, which is usually user-defined based on the specific application, can influence the estimate of peak power.

The estimation result of peak discharge current and peak discharge power by using 1 s, 20 s, and 60 s as prediction time horizon is shown in Figure 3.13. As shown, the peak discharge current and power are high at the beginning and drops gradually. This is because the SOC and terminal voltage is high at the initial stage, and a very large discharge current is allowed to bring the terminal voltage or SOC to the lower cut-off value. As the hybrid pulse experiment proceeds, both SOC and the terminal voltage drops significantly, thus a smaller discharge current will be adequate for the battery to reach the lower cut-off thresholds. We also observe that the peak discharge current and peak discharge power decrease remarkably when increasing the prediction time horizon. This feature can be explained by the voltage response

under current excitation within the selected prediction time horizon, as shown in Figure 3.14. As shown, two charging current pulses with different magnitudes are imposed on the battery at time t_0 , and the corresponding voltage responses are V_1 and V_2 , respectively. It is observed that V_1 and V_2 arrive the voltage upper limit after 60 s and 1 s, respectively. In this regard, the peak current will be I_1 if we select the time horizon as 60 s. Instead, the time horizon of 1 s will allow I_2 as the peak current, which is observed to be much larger than I_1 .

Figure 3.13 Estimation results of peak discharge current and peak discharge power by using different prediction time horizons (ignoring the design current limit)

Figure 3.14 Interpretation of the peak current when different time horizons are selected

Figure 3.15 Estimation results of peak charge current and peak charge power by using different prediction time horizons (ignoring the design current limit)

The estimation result of peak charge current and peak charge power by using 1 s, 20 s, and 60 s as prediction time horizon is shown in Figure 3.15. It is found that the peak charge current and peak charge power both increases in magnitude as the

hybrid pulse experiment proceeds, which can be explained by the fact that a large charge current in magnitude is permitted for the terminal voltage and SOC to reach the upper cut-off value at a low SOC. The influence of prediction time horizon on the peak charge current/power is the same as that on the discharge case, and the similar explanations apply to this phenomenon.

3.5.4 Peak Power Estimation by Multi-constraints

The design current limit serves as another constraint for the peak power. The mass-transfer controlled limiting current is commonly used as the constraint in the literatures [137, 139]. However, it is not recommended to apply a large current that approaches the limiting current in practical applications. There are majorly two reasons for this. Firstly, as the current increases, the concentration overpotential enhances significantly and leads to large declines of both output power and efficiency. Secondly, the use of small current contributes to elongating the battery life calendar. Experiments have been done to study the effect of load current on energy efficiency and capacity decay. The results show that a load current larger than 8 A for the 100 cm² VRB cell (equivalent to 80 mA cm⁻²) is unfavorable to the VRB performance in long-term operation. Therefore, we adopt a constant value of 8 A as the design current limit in this chapter.

In this section, the design current limit is accounted for to perform the peak power estimation by multi-constraints. Taking the discharge case as instance, if the design limit of the discharge current is higher than the peak discharge current shown in Figure 3.13, it will not take effect and the estimation result will be identical with that discussed in Section 3.5.3. Otherwise, the design current limit will be in effect and the estimation result will be different.

By considering the design current limit in Table 3.5, the estimated peak discharge current and peak discharge power are shown in Figure 3.16. It is clear that the peak discharge current follows different constraints at different stages. During t_1 , the design current limit is the lowest among the three constraints and acts as the major constraint. Therefore, the estimated peak discharge power during this stage reduces significantly compared with that shown in Figure 3.13. The estimated peak

discharge power is also much more stable than that in Figure 3.13 as the peak discharge current is constant at 8 A in this case. After that, the voltage-constrained peak discharge current drops below the design limit and begins to take effect during t_2 . During t_3 when the SOC approaches the lower bound, the SOC-constrained peak discharge current which is quite high before starts to drop sharply to become the lowest one, thus behaves as the major constraint. During t_2 and t_3 , the design current limit is not in effect so that the estimated peak discharge power in Figure 3.16 (c) is identical with that in Figure 3.13. It is shown that the proposed method can effectively synthesize and coordinate different constraints thus make the optimized estimation which will be more reliable in practical applications.

The estimated peak charge current considering multiple constraints is shown in Figure 3.17 (a, b). Analogously, the three constraints dominate at different stages. At the very beginning (t_1), the SOC is close to the upper bound so that the battery can only tolerate quite small charge current (in magnitude) to avoid over-charge. For this reason, the SOC-constrained peak charge current is the major concern at this stage. After this, the SOC-constrained peak charge current increases drastically (in magnitude) and the terminal voltage becomes the major constraint. As the voltage-constrained peak charge current exceeds the design current limit, the latter one starts to be the major constraint. The corresponding multi-constrained peak charge power by using different prediction time horizons is plotted in Figure 3.17 (c). The estimated peak charge power during t_1 and t_2 is consistent with that shown in Figure 3.15, as the design current limit has not taken effect at this time. After that, the charge power decreases mildly and stably in magnitude during t_3 . This is because the peak charge current is fixed at -8 A at this stage and the corresponding terminal voltage decreases slowly as the hybrid pulse experiment proceeds.

It should be clarified that the proposed method estimates the peak power of VRB stack. The VRB systems in real applications may also be self-feeding, i.e. using the stack power output to run the pumps. In this case, the pumping power loss which is strongly dependent on operating flow rate should be deducted from (for peak discharge power estimation) or added to (for peak charge power estimation) the estimated peak power based on the proposed method.

Figure 3.16 Estimation results of peak discharge current and peak discharge power: (a) peak discharge current by single constraints and multiple constraints; (b) zoom figure of (a) with a small range of y axis; (c) peak discharge power by using different prediction time horizons

Figure 3.17 Estimation results of peak charge current and peak charge power: (a) peak charge current by single constraints and multiple constraints; (b) zoom figure of (a) with a small range of y axis; (c) peak charge power by using different prediction time horizons

3.5.5 Discussion on the influence of flow rate and temperature

The temperature and flow rate are key operating parameters to influence the performance of VRB. The peak power estimation can be affected by these factors in two different ways.

Firstly, the physical and chemical processes of VRB are affected by both temperature and flow rate so that the model parameters which are involved in the peak power calculation are also subject to changes. Therefore, the model-based peak power estimation is surely relevant to these factors. However, this effect can be well addressed by the proposed method. It is known that the changes of operating variables and thus model parameters can be reflected in the current-voltage response. As a data-driven method, the proposed method can dig into the current-voltage characterization and update the model parameters continuously in real time. For this advantage, the proposed estimator can fully adapt to the change of these factors.

Secondly, the mass-transfer limitations between the bulk electrolyte solution and the electrode surface are highly dependent on the volumetric flow rate. The limiting current is governed by the bulk concentration and the rate of mass transfer of vanadium ions from the bulk solution to the electrode surface, and can be expressed by [139]:

$$I_{\text{lim}} = nFA_m k_m C_b \quad (3.28)$$

where n is the electrons involved in the redox reaction, F is the Faraday's constant, A_m is the cross-sectional area of the porous flow-through electrode, C_b is the bulk concentration of vanadium ions in solution, k_m is the local mass transfer coefficient which can be approximated by:

$$k_m = 1.6 \times 10^{-4} v_e^{0.4} \quad (3.29)$$

where v_e is the electrolyte flow velocity through the rectangular channel.

Under specific cell design and electrolyte concentration, it is clear that the limiting

current is dependent on the volumetric flow rate and SOC. In other words, it is actually time variant with the change of working condition. In this chapter, in seeking to improve the efficiency and to extend the battery life, we apply a constant current limit of 8 A for the 100 cm² VRB cell which actually simplifies the peak power estimation. In our future work, the limiting current expressed by Eq. (3.28) will be applied in the viewpoint of fully exploiting the VRB power. To achieve this, mathematical models considering the mass transfer and concentration overpotential effect will be built and integrated into the proposed estimator.

3.6 Conclusions

This chapter proposes an online peak power estimator based on an adaptive battery model for VRB. The OCV is measured with an open-circuit cell and the other model parameters are online identified with both RLS and EKF for comparison. Based on the online identified battery model, an adaptive estimator is proposed which incorporates the constraints of voltage, SOC, and current to estimate the real-time peak power for the given prediction time horizon.

The key findings are summarized as follows: (1) the RLS proves to outperform the EKF for online model identification by assessing the identification accuracy, convergence speed, and computational cost; (2) the RLS-based online identified battery model is experimentally verified to model the VRB dynamics with high accuracy; (3) the peak current calculation and the power sequence estimation under the peak current are verified with the “two-step verification” method, in which way the proposed peak power estimator is verified; (4) the experimental result suggests that different constraints dominate the determination of peak power at different stages, and the proposed estimator can well coordinate them and realize the multi-constrained estimation which is more reliable; (5) the estimated peak power depends largely on the selection of the prediction time horizon.

CHAPTER 4 Online Model Identification and State of Charge Estimation for Vanadium Redox Flow Battery with a Multi-timescale Estimator

4.1 Introduction

Extensive studies aimed at the improvement of cell performance, mainly in the field of electrode modification, membrane enhancement, and electrolyte solution update [147-149] have been conducted. Some important issues of the VRB technology in real applications have yet to be adequately addressed however. The SOC, as one important state to be monitored in BMS, is essential to assess the battery condition and to avoid over-charge and/or over-discharge.

The electrochemical methods by Skyllas-Kazacos et al. [74, 75], which have been reviewed in Section 2.4.3 C monitor the SOC of each half-cell and aim at detecting any imbalance between the two individual half-cell electrolytes that would lead to capacity loss. In real applications, the overall SOC of the cell is also vital considering its implication on the short- and long-term energy management. Regarding online SOC determination, OCV measurement as adopted in Chapter 3 is straightforward and has been widely used in commercial products [146]. However, additional open-circuit cells and sensors need to be installed thus adding more complexity to the battery configuration. Furthermore, the open-circuit cell approach can only be used for flow batteries where the electrolytes are stored in external reservoirs and pumped through a cell stack where the charge-discharge reactions take place. Other methods like the CC technique have also reviewed in Section 2.4.3 with the drawbacks clarified.

In recent works [41-51], SOC was estimated in real time for lithium-ion batteries by the ECM based observers, which are also promising to be applied on VRB. This category of methods is fundamentally achieved with two steps. First, an accurate model is established to reproduce the transient behavior of battery. The existing

ECMs for battery research and those intended specifically for VRB have been reviewed in Section 2.4.2, thus they will not be further introduced here. In the second step, the adaptive filters, such as EKF [41-43], UKF [43, 44], PF [45-47], and some other extensions [48-51], are applied to observe the SOC. Such ECM-based observers effectively overcome the shortcomings of the SOC-OCV mapping and CC technique. One common feature of the methods is that the model parameters are prescribed offline and left without adaption during operation. However, as the model parameters are actually changing with both working conditions and self-aging, the non-adaption of them will degrade the accuracy and cause the estimator to lose robustness. For this reason, the online identification of model parameters has been focused recently, albeit limited, to improve the precision of SOC estimation. In the existing studies, the model parameters and SOC/OCV are integrated together for joint estimation [59, 136, 150] or dual estimation [95, 151-153]. However, the integration can cause cross interference between the model parameters and SOC/OCV and thus substantially compromise the regression stability. The joint estimation can also cause large-scale matrices calculation and accordingly brings more parameterization effort and even leads to instability issues.

In this chapter, a novel multi-timescale estimator is proposed to online adapt the model parameters and estimate the battery SOC simultaneously. The proposed method is data-driven type and is free from the constraint of using additional open-circuit cells for OCV determination, which is a key improvement of the model used in Chapter 3. Unlike other traditional methods, the OCV and model parameters are identified with three independent estimators to avoid the cross interference, while SOC is estimated with the look-up table of SOC versus OCV. As another merit, the SOC estimator is implementable without exact information of the cell capacity, which is indispensable in most of existing ECM-based observers. Theoretical analysis on sensitivity, stability and precision is executed to explore the performances of each independent estimator. Based on this, different timescales are applied to enhance each estimator and to release computational burden.

The rest of the chapter is organized as follows. Section 4.2 presents the OCV estimator and associated sensitivity analysis. Section 4.3 discusses the identification

of model parameters and proposes the multi-timescale estimator based on the analysis of model precision and stability. Section 4.4 describes the experimental setup and details. The algorithm verification is presented in Section 4.5 and the key conclusions of this chapter are drawn in Section 4.6.

4.2 Independent OCV Estimator

4.2.1 Battery Modeling

To simplify the battery model configuration to the greatest extent while keeping sufficient precision, the first-order RC model which has been widely used for lithium-ion and NiMH battery is adopted in this thesis. It has to be mentioned however, that the method proposed here is applicable to a broad range of higher-order battery models. The model structure can be found in Figure 3.1. It has to be noted that the SOC- and temperature-dependent OCV is no longer measured with the open-circuit cell as in Chapter 3; otherwise, it is online estimated with an OCV estimator in this chapter.

4.2.2 OCV Estimation

Instead of using the open-circuit cell as in Chapter 3, in this section, an independent OCV estimator using only onboard measured current and voltage is introduced. The electrical behavior of the first-order RC model is expressed as Eq. (3.1) and Eq. (3.2), from which the following discrete-time form can be written:

$$V_p(t) = e^{-\frac{nt_s}{R_p C_p}} V_p(t - nt_s) + (1 - e^{-\frac{t_s}{R_p C_p}}) R_p \sum_{j=1}^n e^{-\frac{(j-1)t_s}{R_p C_p}} I_L(t - jt_s) \quad (4.1)$$

where t_s is the sampling time of onboard data, and n denotes the user-defined sampling interval used to update the OCV. Thus, the timescale of the OCV estimator (Δt_1) can be calculated as $\Delta t_1 = nt_s$. At any time step, the below relationship holds according to Eq. (3.2):

$$V_p(t - nt_s) = V_{oc}(t - nt_s) - V_t(t - nt_s) - I_L(t - nt_s)R_s \quad (4.2)$$

Substituting Eq. (4.2) into Eq. (4.1) yields:

$$\begin{aligned} V_{oc}(t) = & e^{-\frac{nt_s}{R_p C_p}} V_{oc}(t - nt_s) - e^{-\frac{nt_s}{R_p C_p}} [V_t(t - nt_s) + I_L(t - nt_s)R_s] \\ & + (1 - e^{-\frac{t_s}{R_p C_p}}) R_p \sum_{j=1}^n e^{-\frac{(j-1)t_s}{R_p C_p}} I_L(t - jt_s) + V_t(t) + I_L(t)R_s \end{aligned} \quad (4.3)$$

Eq. (4.3) can be alternatively expressed in a linear form as:

$$y(t) = \phi^T(t)u(t) + \varepsilon_1(t) \quad (4.4)$$

where

$$\begin{aligned} \phi(t) &= V_{oc}(t) \\ u(t) &= 1 - e^{-\frac{nt_s}{R_p C_p}} \\ y(t) &= V_t(t) + I_L(t)R_s - e^{-\frac{nt_s}{R_p C_p}} [V_t(t - nt_s) + I_L(t - nt_s)R_s] \\ &+ (1 - e^{-\frac{t_s}{R_p C_p}}) R_p \sum_{j=1}^n e^{-\frac{(j-1)t_s}{R_p C_p}} I_L(t - jt_s) \\ \varepsilon_1(t) &= e^{-\frac{nt_s}{R_p C_p}} [V_{oc}(t) - V_{oc}(t - nt_s)] \end{aligned} \quad (4.5)$$

$V_{oc}(t)$ is treated as the time varying parameter to be identified. The model input $u(t)$ is only related to the model parameters waiting for further identification. The model output $y(t)$ depends on both the model parameters and onboard measured current/voltage. Based on the regression model with Eq. (4.4), the OCV can be estimated online with the RLS method. Details about the RLS algorithm are not elaborated here but can be referred to existing literatures [143]. Once OCV is obtained, the battery SOC can be easily determined with the look-up table between OCV and SOC.

4.2.3 Precision and Stability

The model precision depends on whether the error term $\varepsilon_1(t)$ is ignorable with respect to $y(t)$. It is known that the battery OCV variation is considerably small within a short time interval. Specifically, the OCV drops from around 1.53 V to 1.29 V when VRB is discharged from 90% (SOC) to 10% (SOC). Within a sufficiently small Δt_1 , it is reasonable to confirm $V_{oc}(t) \approx V_{oc}(t - nt_s)$ thus $\varepsilon_1(t)$ approximates zero. To this end, a small Δt_1 is plausible. The stability can be easily confirmed as the model is zero order.

4.2.4 Sensitivity Studies

The precision of OCV estimator will degrade when the model parameters are subject to identification errors. Within this context, the sensitivity of the OCV estimator to the error on each model parameter is worth investigating. With identification errors on the model parameters, Eq. (4.4) becomes:

$$\hat{y}(t) = \phi^T(t)\hat{u}(t) + \hat{\varepsilon}_1(t) \quad (4.6)$$

where $\hat{y}(t)$ is the observation of $y(t)$ when identification errors exist and vice versa for $\hat{u}(t)$ and $\hat{\varepsilon}_1(t)$. As $\varepsilon_1(t)$ itself is negligible compared with the other terms, it is reasonable to assume that the identification errors have negligible impacts on it and thus $\hat{\varepsilon}_1(t) \approx \varepsilon_1(t)$. By transposition, the below expression can be drawn:

$$y(t) = \phi^T(t)u(t) + \varepsilon_1(t) + \Lambda\varepsilon_1(t) \quad (4.7)$$

where $\Lambda\varepsilon_1(t)$ corresponds to the additional error term caused by the identification errors on model parameters and can be expressed as:

$$\Lambda\varepsilon_1(t) = y(t) - \hat{y}(t) + \phi^T(t)\hat{u}(t) - \phi^T(t)u(t) \quad (4.8)$$

where $\hat{u}(t)$ and $\hat{y}(t)$ can be expressed as:

$$\begin{aligned}
 \hat{u}(t) &= 1 - e^{-\frac{nt_s}{(R_p + R_p)(C_p + \Delta C_p)}} \\
 \hat{y}(t) &= V_t(t) + I_L(t)(R_s + \Delta R_s) \\
 &\quad - e^{-\frac{nt_s}{(R_p + \Delta R_p)(C_p + \Delta C_p)}} [V_t(t - nt_s) + I_L(t - nt_s)(R_s + \Delta R_s)] \\
 &\quad + (1 - e^{-\frac{t_s}{(R_p + \Delta R_p)(C_p + \Delta C_p)}})(R_p + \Delta R_p) \sum_{j=1}^n e^{-\frac{(j-1)t_s}{(R_p + \Delta R_p)(C_p + \Delta C_p)}} I_L(t - jt_s)
 \end{aligned} \tag{4.9}$$

where ΔR_s , ΔR_p and ΔC_p are the identification errors on model parameters. A new term defined as $\Delta V_{oc}(t) = \Delta \varepsilon_1(t)/u(t)$ is used here to quantitatively evaluate the variation of OCV estimation caused by the additional error. The definition is fundamentally derived from Eq. (4.7). It should be noted however that $\Delta V_{oc}(t)$ is not strictly equal to the real OCV variation in real recursive estimation where the RLS filter is used to smooth the regression. However, the defined $\Delta V_{oc}(t)$ can still give deep insight into how the identification errors on model parameters degrade the OCV estimator.

To give a perspective, the following two conditions are used to simulate the influence of identification errors on the additional error term ($\Delta \varepsilon_1$) and OCV variation (ΔV_{oc}):

Condition 1: $\Delta t_1 = 1$ s, $R_s = 19$ m Ω , $R_p = 2.5$ m Ω , $C_p = 8$ kF, OCV = 1.4242 V, $I_L(t) = I_L(t - \Delta t_1) = 2.4$ A, $V(t) \approx V(t - \Delta t_1) = 1.3783$ V;

Condition 2: $\Delta t_1 = 1$ s, $R_s = 19$ m Ω , $R_p = 2.5$ m Ω , $C_p = 8$ kF, OCV = 1.4242 V, $I_L(t - \Delta t_1) = -0.8$ A, $I_L(t) = 2.4$ A, $V(t - \Delta t_1) = 1.4434$ V, $V(t) = 1.3814$ V;

The two conditions are both from real experimental data at SOC around 53%. Condition 1 represents a stationary load current condition, while condition 2 describes a current jump at the present time step. The assumed model parameters are selected according to the hybrid pulse test which will be presented in Section 4.4. Simulations are performed and the results are shown in Figure 4.1. It can be summarized that: (1) The OCV estimator is most sensitive to the identification error on R_s ; (2) The impact of identification errors is not negligible. The OCV variation

can reach up to 45 mV with 10% identification error on R_s . (3) Compared with stationary current condition, the OCV estimator is much more sensitive to identification errors under a dynamic current condition which is more common in real applications. The sensitivity studies allow a deeper understanding about the OCV estimator and serve as an important guide for the design of model parameter estimator.

Figure 4.1 Sensitivity of the OCV estimator to the identification errors on model parameters: (a, c) stationary current condition; (b, d) varying current condition

4.3 Online Adapted Model and Multi-timescale Estimator

4.3.1 Online Model Parameters Identification

As indicated in the sensitivity analysis, the precision and stability of R_s identification is vital to the OCV estimator, as a result of which the identification of R_s should be given more emphasis. Again, to prohibit the cross interference between different model parameters, R_s is identified independently rather than integrated with R_p and C_p in the same vector. From Eq. (3.2), the below relationship is established:

$$\begin{aligned} \Delta V_i(t) &= -R_s \Delta I_L(t) + \varepsilon_2(t) \\ \text{where } \varepsilon_2(t) &= \Delta V_{oc}(t) - \Delta V_p(t) \end{aligned} \quad (4.10)$$

where $\Delta V_i(t)$ is defined as the differential voltage, expressed by $V_i(t) - V_i(t - \Delta t_2)$, and Δt_2 denotes the timescale used to calculate and update R_s . The analogous definition applies to the other terms. Through this way, R_s can also be updated with the RLS method.

The stability is easily confirmed considering the one-dimensional parameter vector and regressor are involved. The error term $\varepsilon_2(t)$ is determined by both $\Delta V_{oc}(t)$ and $\Delta V_p(t)$. Generally, $\varepsilon_2(t)$ decreases by shortening the timescale Δt_2 as the variation of OCV tends to be subtle. Regardless of Δt_2 however, $\varepsilon_2(t)$ can be in the same order with model output $\Delta V_i(t)$ if the current variation $\Delta I_L(t)$ is too small. The feasibility of this method thereafter depends on two prerequisites: (1) Δt_2 is sufficiently small; (2) R_s is only updated under the situation that $|\Delta I_L(t)| \geq \xi$ with ξ as a user-defined threshold to trigger the update of R_s .

By using different time resolution, Eq. (4.1) can be expressed in a new form as:

$$V_p(t) = e^{-\frac{\Delta t_3}{R_p C_p}} V_p(t - \Delta t_3) + (1 - e^{-\frac{\Delta t_3}{R_p C_p}}) R_p I_L(t - \Delta t_3) \quad (4.11)$$

where Δt_3 is the timescale of the R_p and C_p estimation. Meanwhile, from Eq. (3.2)

we also have:

$$V_p(t) = V_{oc}(t) - V_t(t) - I_L(t)R_s \quad (4.12)$$

Substituting Eq. (4.12) into Eq. (4.11) yields:

$$V_t(t) + I_L(t)R_s = V_{oc}(t) - \alpha_1 V_{oc}(t - \Delta t_3) + \alpha_1 V_t(t - \Delta t_3) + \alpha_2 I_L(t - \Delta t_3) \quad (4.13)$$

where

$$\begin{bmatrix} \alpha_1 & \alpha_2 \end{bmatrix} = \begin{bmatrix} e^{-\frac{\Delta t_3}{R_p C_p}} & R_s e^{-\frac{\Delta t_3}{R_p C_p}} - (1 - e^{-\frac{\Delta t_3}{R_p C_p}})R_p \end{bmatrix} \quad (4.14)$$

Shifting Eq. (4.13) to the previous time step yields:

$$\begin{aligned} V_t(t - \Delta t_3) + I_L(t - \Delta t_3)R_s &= V_{oc}(t - \Delta t_3) - \alpha_1 V_{oc}(t - 2\Delta t_3) \\ &\quad + \alpha_1 V_t(t - 2\Delta t_3) + \alpha_2 I_L(t - 2\Delta t_3) \end{aligned} \quad (4.15)$$

By subtracting Eq. (4.15) from Eq. (4.13), the following equation can be drawn:

$$\begin{aligned} \Delta[V_t(t) + I_L(t)R_s] &= \Delta[V_{oc}(t) - \alpha_1 V_{oc}(t - \Delta t_3)] \\ &\quad + \alpha_1 \Delta V_t(t - \Delta t_3) + \alpha_2 \Delta I_L(t - \Delta t_3) \end{aligned} \quad (4.16)$$

where $\Delta[V_t(t) + I_L(t)R_s]$ is defined as the differential polynomial expressed by $[V_t(t) + I_L(t)R_s - (V_t(t - \Delta t_3) + I_L(t - \Delta t_3)R_s)]$, and the analogous definition applies to the other terms. Alternatively, Eq. (4.16) can be expressed in a regression form as:

$$y_3(t) = \phi_3^T(t)u_3(t) + \varepsilon_3(t) \quad (4.17)$$

where

$$\begin{aligned} \phi_3(t) &= [\alpha_1 \quad \alpha_2]^T \\ u_3(t) &= [\Delta V_t(t - \Delta t_3) \quad \Delta I_L(t - \Delta t_3)]^T \\ y_3(t) &= \Delta[V_t(t) + I_L(t)R_s] \\ \varepsilon_3(t) &= \Delta[V_{oc}(t) - \alpha_1 V_{oc}(t - \Delta t_3)] \end{aligned} \quad (4.18)$$

Again, the regression model can be solved with RLS. Then R_p and C_p are reversely solved as:

$$\begin{bmatrix} R_p & C_p \end{bmatrix} = \begin{bmatrix} \frac{\alpha_2 - R_s \alpha_1}{\alpha_1 - 1} & \frac{(1 - \alpha_1) \Delta t_3}{(\alpha_2 - R_s \alpha_1) \ln \alpha_1} \end{bmatrix} \quad (4.19)$$

With the online extracted model parameters, the terminal voltage at the next onboard sampling time can be modeled as:

$$\begin{aligned} V_t(t + t_s) = & V_t(t) + e^{-\frac{t_s}{R_p C_p}} \Delta V_t(t) \\ & + [R_s e^{-\frac{t_s}{R_p C_p}} - (1 - e^{-\frac{t_s}{R_p C_p}}) R_p] \Delta I_L(t) - \Delta I_L(t) R_s \end{aligned} \quad (4.20)$$

4.3.2 Precision and Stability

The precision and stability of the regression model (4.10) and (4.17) are largely determined by the selection of timescale Δt_2 and Δt_3 . It is clear that the error terms $\varepsilon_2(t)$ and $\varepsilon_3(t)$ both approximate zero when the corresponding timescale approaches zero. Therefore, it is plausible to set Δt_2 and Δt_3 to the minimum value allowable to constrain the modeling error terms.

Eq. (4.10) represents a zero-order system with its stability easily guaranteed regardless of Δt_2 . In contrast, the stability of the model (4.17) is a bit more complicated. Eq. (4.16) can be alternatively expressed as the form of:

$$\Delta V_t(k) = \alpha_1 \Delta V_t(k-1) + \alpha_2 \Delta I_L(k-1) + \Phi(k) \quad (4.21)$$

where k is the index of the present time step. $\Delta V_t(k)$ and $\Delta I_L(k)$ are respectively treated as the system output and input. $\Phi(k)$ is the disturbance calculated as $\Phi(k) = \varepsilon_3(k) - \Delta I_L(k) R_s$. The transfer function of system represented by Eq. (4.21) can be expressed as:

$$G(z^{-1}) = \frac{\alpha_2 z^{-1}}{1 - \alpha_1 z^{-1}} \quad (4.22)$$

where z is the discretization operator. Stability requires all poles to be placed inside the unit circle of z plane. For the present case, the pole is solved as α_1 which depends closely on Δt_3 . In order to evaluate the influence of Δt_3 on system stability, a simulation study was carried out. The following two parameter sets representing different operating conditions are illustrated:

Condition 1: $R_s = 19 \text{ m}\Omega$, $R_p = 2.5 \text{ m}\Omega$, $C_p = 8 \text{ kF}$ (typical data for flow rate of 120 mL min^{-1} and middle SOC region);

Condition 2: $R_s = 25 \text{ m}\Omega$, $R_p = 14 \text{ m}\Omega$, $C_p = 3 \text{ kF}$ (typical data for flow rate of 120 mL min^{-1} and low SOC region);

The model parameters are selected with based on the hybrid pulse test. The pole coordinates with different selections of Δt_3 are summarized in Table 4.1. The result shows that the pole moves towards zero inside the unit circle as Δt_3 increases, which suggests an enhanced stability. Especially, the stability is substantially attenuated at the low SOC region, reflected by the large poles under condition 2. Summarily, the model is more vulnerable to the perturbations and model uncertainties with a small time scale especially within low SOC region. Within this context, a large Δt_3 is desirable to stabilize the model under a wide range of conditions.

Table 4.1 Pole coordinates with different selections of Δt_3

	Δt_3						
	0.5	1	2	3	4	5	6
Pole (Condition 1)	0.975	0.951	0.905	0.861	0.819	0.779	0.741
Pole (Condition 2)	0.988	0.977	0.954	0.931	0.909	0.888	0.967

4.3.3 Multi-timescale Model Parameter Identification

In this chapter, the OCV estimator and model parameter estimator are fully decoupled. As an outstanding merit, the decoupling treatment allows selecting different timescales to enhance each estimator independently. According to the analysis on model precision and stability, Δt_1 and Δt_2 are both set as 1 s which is

equal to the onboard sampling time to maximize the model precision, while a larger timescale $\Delta t_3 = 4$ s is selected for R_p and C_p estimation regarding the trade-off between precision and stability. The detailed algorithm of the multi-timescale estimator is summarized in Table 4.2.

4.4 Experimental Details

4.4.1 Experimental Setup

The schematic of the experimental setup is the same as Figure 3.7. The only difference is that the measured OCV is only for verification purpose and will not be used by the proposed multi-timescale estimator. The ambient temperature was monitored to be stable at $22\pm 1^\circ\text{C}$ throughout the tests. Experiments under different operating flow rates are realized by adjusting the two peristaltic pumps.

4.4.2 Battery Tests

A. SOC-OCV Test and Sensitivity Analysis

The SOC-OCV test is performed with the procedures described in Section 3.4.2. To assess the OCV curve variation with respect to battery aging, several OCV tests were conducted at different aging states and the results are shown in Figure 4.2. It should be mentioned that the battery is cycled with very deep charge and discharge or even over-charge and over-discharge, which is actually not recommended in real applications, in order to accelerate the aging as soon as possible. During this period, the capacity dropped from 3293.6 mAh to 3078.1 mAh. The capacity fade of 6.54% represents a substantial aging in real applications. It is observed that the SOC-OCV curve of VRB is not sensitive to the battery aging. For the SOC range from 10% to 95% which corresponds to the typical operating range of VRB, the OCV variation is only 1.562 mV. Therefore, the SOC-OCV look-up table can be used without frequent recalibrations. However, it should be mentioned that this conclusion is applicable to the aging degree presented in this section. Recalibration may be needed if the aging is too severe.

Table 4.2 Algorithm details of the multi-timescale estimator

Initialization: $\hat{\phi}_1(0), P_{\phi_1}(0); \hat{R}_s(0), P_R(0); \hat{\phi}_3(0), P_{\phi_3}(0);$

For $k = 1, 2, 3, \dots$

Step 1: Priori parameter and covariance matrix update for θ ,

$$\hat{\phi}_3^-(k) = \hat{\phi}_3^+(k-1), \quad P_{\phi_3}^-(k) = P_{\phi_3}^+(k-1) \quad (4.23)$$

For $m = 1, 2, 3, \dots, \Delta t_1 (\Delta t_2)$

Step 2: Priori parameter and covariance matrix update for R_s ,

$$\hat{R}_s^-(k, m) = \hat{R}_s^+(k, m-1), \quad P_R^-(k, m) = P_R^+(k, m-1) \quad (4.24)$$

Step 3: Gain, posterior parameter and covariance matrix update for R_s :

if $|\Delta I_L(k)| > \xi$

$$\begin{aligned} L_R(k, m) &= P_R^-(k, m)(-\Delta I_L(k, m)) \left[\lambda_R + (-\Delta I_L^T(k, m)) P_R^-(k, m)(-\Delta I_L(k, m)) \right]^{-1} \\ \hat{R}_s^+(k, m) &= \hat{R}_s^-(k, m) + L_R(k, m) \left[\Delta V_i(k, m) - \hat{R}_s^-(k, m)(-\Delta I_L(k, m)) \right] \\ P_R^+(k, m) &= \left[I - L_R(k, m)(-\Delta I_L^T(k, m)) \right] P_R^-(k, m) \lambda_R^{-1} \end{aligned} \quad (4.25)$$

else

$$\hat{R}_s^+(k, m) = \hat{R}_s^-(k, m), \quad P_R^+(k, m) = P_R^-(k, m) \quad (4.26)$$

Step 4: Priori parameter and covariance matrix update for ϕ ,

$$\hat{\phi}_1^-(k, m) = \hat{\phi}_1^+(k, m-1), \quad P_{\phi_1}^-(k, m) = P_{\phi_1}^+(k, m-1) \quad (4.27)$$

Step 5: Gain, posterior parameter and covariance matrix update for ϕ ,

$$\begin{aligned} L_{\phi_1}(k, m) &= P_{\phi_1}^-(k, m) u_1(k, m) \left[\lambda_{\phi_1} + u_1^T(k, m) P_{\phi_1}^-(k, m) u_1(k, m) \right]^{-1} \\ \hat{\phi}_1^+(k, m) &= \hat{\phi}_1^-(k, m) + L_{\phi_1}(k, m) \left[y_1(k, m) - \hat{\phi}_1^-(k, m) u_1(k, m) \right] \\ P_{\phi_1}^+(k, m) &= \left[I - L_{\phi_1}(k, m) u_1^T(k, m) \right] P_{\phi_1}^-(k, m) \lambda_{\phi_1}^{-1} \end{aligned} \quad (4.28)$$

Step 6: Timescale transition,

if $m = \Delta t_1 (\Delta t_2)$

$$\hat{R}_s^+(k+1, 0) = \hat{R}_s^+(k, \Delta t_2); \hat{\phi}_1^+(k+1, 0) = \hat{\phi}_1^+(k, \Delta t_1) \quad (4.29)$$

else return to Step 2

End for the inner cycle

Step 7: Gain, posterior parameter and covariance matrix update for θ :

$$\begin{aligned} L_{\phi_3}(k, m) &= P_{\phi_3}^-(k, m) u_3(k, m) \left[\lambda_{\phi_3} + u_3^T(k, m) P_{\phi_3}^-(k, m) u_3(k, m) \right]^{-1} \\ \hat{\phi}_3^+(k, m) &= \hat{\phi}_3^-(k, m) + L_{\phi_3}(k, m) \left[y_3(k, m) - \hat{\phi}_3^-(k, m) u_3(k, m) \right] \\ P_{\phi_3}^+(k, m) &= \left[I - L_{\phi_3}(k, m) u_3^T(k, m) \right] P_{\phi_3}^-(k, m) \lambda_{\phi_3}^{-1} \end{aligned} \quad (4.30)$$

End for the outer cycle

Figure 4.2 Polynomial fitting of OCV versus SOC under different aging states

Figure 4.3 Load current, terminal voltage and recorded SOC obtained from the pulse discharging experiment

B. Hybrid Pulse Experiment

To verify the feasibility and robustness of the proposed multi-timescale estimator, a pulse discharge experiment was performed with the current, terminal voltage and SOC data plotted in Figure 4.3.

C. Offline Model Parameters Identification

In order to verify the accuracy of online model parameters identification, the reference values of model parameters should be determined. The HPPC method is typically used for the offline model parameter calibration of lithium-ion batteries. In this chapter, as the hybrid pulse experiment contains lots of current pulses which are similar to those from the HPPC method, we extract the reference model parameters directly from the hybrid pulse experiment profile.

During the hybrid pulse experiment, several batches of current and voltage data are sampled around specific time points. Then the reference model parameters are extracted offline by fitting the modeled terminal voltages to the measured data. The extraction can be achieved with a wide range of optimization methods such as evolutionary algorithms [154]. In this chapter, however, the batch LS method was adopted.

4.5 Verification and Discussion

4.5.1 Model Parameters Identification

The model parameters are estimated online at the respective time step. To show the robustness of the algorithm against unknown initializations, erroneous initial values are intentionally set as follows: $R_s = 0 \text{ m}\Omega$, $R_p = 1 \text{ m}\Omega$, and $C_p = 2 \text{ kF}$. The forgetting factor of the R_s estimator is 0.98, while the R_p and C_p estimator uses a much larger forgetting factor of 0.999.

Figure 4.4 Results of the model parameters identification

The estimated model parameters versus SOC are plotted in Figure 4.4 in comparison with their reference values determined offline. As shown, the identified results quickly converge to their true values after limited steps for erroneous initialization correction and keep tracking them continuously. Specifically, R_s is parameterized with a higher stability and precision, mostly because the internal resistance is only related to the instantaneous voltage change under a current variation. By comparison, the identification of the other two parameters especially for C_p is more fluctuated. This can be explained by the fact that the polarization resistance and capacitance are more dependent on the complicated physiochemical process of VRB under current excitation, which is quite difficult to be simulated. It is also observed that the identification lags the real parameter variation to some

extent at low SOC regions (<10%), mainly because non-zero forgetting factors are used for the purpose of algorithm stabilization. However, VRB is seldom operated under such situations in real applications to prevent over-discharge and cell reversal. In summary, the proposed multi-timescale estimator is reliable in adaptively tracking the variations of the model parameters with sufficient robustness against the initialization uncertainties.

With the online extracted model parameters, the modeled terminal voltage along with the real measured data are shown in Figure 4.5. As can be seen, even though the CPE and Warburg impedance term are omitted for simplification, the model outputs still match the measured terminal voltage quite closely with subtle errors. The modeling error is constrained within 2 mV for most of the time. The maximum error occurs at the extremely low SOC region is around 7 mV, which can be explained by the sharp OCV drop. Obviously, the fast dropping OCV violates the assumption $\Delta[V_{oc}(t) - \alpha_1 V_{oc}(t - \Delta t_3)] \approx 0$, thus the large modelling errors at this region are within expectation. The high modeling accuracy reconfirms the credibility of the online parameterization method and further verifies the reliability of the battery model in online applications.

Figure 4.5 Modelled terminal voltage versus measured data and the modelling error

4.5.2 Online OCV and SOC Estimation

As no prior knowledge of initial OCV was available at the start of experiment, the OCV was erroneously initialized as 1.4 V. The OCV estimator uses a forgetting factor of 0.995. The OCV estimation results are shown in Figure 4.6. As shown, the estimated OCV quickly approximates the reference trajectory after several sampling intervals for correcting the erroneous initialization. The quick convergence is achieved by timely adjusting the RLS feedback according to the error between the measured and estimated terminal voltage. The erroneously estimated OCV leads to a large error in the terminal voltage, which in turn causes a large feedback to compensate the OCV estimation in an efficient closed loop approach. It is observed that the estimation errors in the middle SOC region are always within 3 mV, which is quite accurate in terms of online estimation.

Figure 4.6 Results of online OCV estimation and the estimation error

It is observed that a larger error occurs at the extremely low SOC region and this can be explained from two aspects. Firstly, there is a lagging effect of the recursive

algorithm with non-zero forgetting factor, thus the proposed method converges a bit slowly to the drastically changing OCV at the extremely low SOC region. Secondly, as discussed in Section 4.2.3, the error term $\varepsilon_1(t)$ is ignorable with respect to $y(t)$ in most of the time and this ensures a high estimation accuracy. However, this condition is violated at the end of discharge when the OCV drops largely, so that the relatively large error is within the expectation in this region. In real applications, however, the VRB is seldom operated under such situations in order to avoid over-discharge and prevent cell reversal. As a whole, the overall MAE and MRE are 2.899 mV and 0.207%, respectively, indicating a quite high estimation accuracy. It is thus validated that the proposed multi-timescale estimator is capable of outputting OCV accurately without additional open-circuit cells conventionally applied. The proposed OCV estimator is also robust to incorrect initializations.

Figure 4.7 Results of online SOC estimation and the estimation error

With the updated OCV, battery SOC is determined coincidentally with the look-up table method and the results are shown in Figure 4.7. Similar with OCV estimation,

the estimated SOC converges to the target value quickly even with incorrect guess on the initial SOC. After that, the algorithm keeps on tracing the reference trajectory with small errors which are mostly confined to the 2% error band. The mean and maximum estimation errors are 0.48% and 2.32%, respectively. It is concluded that the proposed method can project the trajectory of SOC accurately with quick convergence, which is highly desirable for BMS. Moreover, the SOC estimation is implemental without any knowledge of the cell capacity, which is demanded in most of the ECM-based SOC observers.

4.5.3 Robustness Analysis against Aging and Flow Rate Variation

This section aims at verifying whether the proposed method is robust against different battery aging states and electrolyte flow rates. To achieve this, the battery is cycled very deeply for several days after the experiments presented in Section 4.5.1 and 4.5.2. During this period, the battery capacity dropped from 3076.8 mAh to 2622.0 mAh as a consequence of different diffusion of vanadium ions across the membrane [110]. The capacity drop of 14.78% has represented a significant aging in real applications. Meanwhile, the electrolyte flow rate was adjusted from the previous 120 mL min⁻¹ to 80 mL min⁻¹. The proposed multi-timescale estimator was executed for the new case for robust performance assessment.

As shown in Figure 4.8 (a-c), the model parameter estimator locates and keeps tracing the true values in a wide SOC range, suggesting satisfactory robustness against aging and flow rate variation. It is also found that the estimated R_s and R_p both increase slightly compared with the previous case. This is within expectation as reducing flow rate increases the concentration overpotential and causes a larger voltage drop under discharging current excitation. Moreover, the more severe concentration overpotential at the end of charge/discharge serves as a strong support on the remarkably enlarged resistances at the extreme low and high SOC regions, as illustrated in Figure 4.8 (a-b). It is clear from Figure 4.8 (d-e) that the modeled terminal voltage is benchmarked with the measured data. The modeling error is confined within 2.5 mV for most of the time, while the larger prediction errors again occur at the end of the discharge.

Figure 4.8 Results of model parameters identification and terminal voltage prediction for the new case: (a-c) online identification results of R_s , R_p and C_p ; (d) comparative profile of measured and predicted terminal voltage; (e) prediction error on terminal voltage; (f) zoom figure of (e)

It is shown from Figure 4.9 that the OCV estimator corrects the initial OCV offset quickly and converges to the target stably with a mean error of 1.970 mV. Similarly, given an erroneous guess of the initial SOC, the estimated SOC can still track the reference trajectory with a sufficiently small mean error of 0.516%. The high estimation accuracy and fast convergence suggest that the proposed multi-timescale estimator has good robustness against the flow rate variation. The robustness to battery aging is also satisfactory within an aging degree of 14.78%. However, it lacks adequate evidences to support the robustness of the proposed method throughout the whole service life as the VRB is reported to have a very long service life of more than 10,000 cycles.

Figure 4.9 Online estimation results of OCV and SOC for the new case: (a) OCV estimation result; (b) OCV estimation error; (c) SOC estimation result; (d) SOC estimation error

4.5.4 Robustness Analysis against Different Battery Chemistries

As the proposed method only utilizes onboard current and voltage data without specific requirements on knowledge of the chemical process, it has potential to be applied for different types of batteries. In this section, the proposed method is also tested on a Samsung 18650 lithium-ion cell with nominal capacity of 2200 mAh to evaluate the robustness performance. The characteristic test of the lithium-ion cell was the same as described in Section 4.4.1 except that the open-circuit cell cannot be used in this case.

It is shown from Figure 4.10 that the model parameters of lithium-ion cell are rather different from those of the VRB. However, the parameters are still accurately adapted with the proposed method. From Figure 4.11, it is found that the transient process of the used lithium cell is more significant than the VRB thus is more difficult to be modeled. Nevertheless, the terminal voltage is still precisely modeled with the online parameterized battery model. The estimation results of OCV and SOC are presented in Figure 4.12 and Figure 4.13, respectively, both of which show fast convergence and high accuracy similar to the case of VRB. The errors of the

terminal voltage modeling, OCV and SOC estimation are summarized in Table 4.3. The results verify that the proposed method can work efficiently with the lithium-ion cell with high precision and fast convergence as well. The robustness against different battery chemistries thus makes it promising for a wide application with other batteries.

Table 4.3 Estimation errors of terminal voltage, OCV and SOC for the lithium-ion cell

	Terminal voltage (mV)	OCV (mV)	SOC (%)
RMSE	0.861	6.593	0.819
Maximum error	32.5	40.004	2.515

Figure 4.10 Results of online model parameters identification for lithium-ion cell

Figure 4.11 Modelling results of terminal voltage and modelling error for the lithium-ion cell

Figure 4.12 Online estimation results of OCV for the lithium-ion cell

Figure 4.13 Online estimation results of SOC for the lithium-ion cell

4.6 Conclusions

A multi-timescale estimator is proposed for the VRB to estimate the time varying model parameters and SOC concurrently in real time. The proposed method has the merits of decoupling different estimation variables thus eliminating the cross interference of estimation between OCV and the other model parameters. The analysis of model sensitivity, precision and stability are put forward to reveal the necessity of employing multiple timescales to improve the overall estimation performance. The dynamic load experiments are performed to verify the real time performance and robustness of the proposed method. The key achievements are summarized as follows: (1) the time varying model parameters are online adapted accurately, thus the frequent recalibration on them is avoided; (2) the modeled terminal voltage from the parameterized battery model is benchmarked with measurement data with subtle error; (3) the online estimation of OCV and SOC shows high convergence speed, high accuracy and good robustness to uncertain initialization; (4) the proposed multi-timescale estimator is robust against the flow

rate variation and its robustness to aging is also satisfactory within an aging degree of 14.78%; and (5) the proposed method is data-driven type using only the onboard measured voltage and current, and it is robust against different battery chemistries.

CHAPTER 5 Adaptive Joint Estimation of State of Charge and Capacity for Vanadium Redox Flow Battery with Online Identified Battery Model

5.1 Introduction

A core function of the BMS is to provide reliable information on SOC and instantaneous capacity. Despite their importance, SOC and capacity determination remains as a challenging task as they are both immeasurable internal states.

The ECM based SOC observers prove to be accurate and implementable. As discussed in Section 4.1, the real-time model adaption has to be executed along with the state estimate to improve accuracy and robustness. The existing methods concerning model parameter and state co-estimation fall into two broad categories. The methods from the first category couple the model parameters and OCV into one vector for joint estimation with either RLS [57, 97, 98] or EKF and its variants [59, 83, 150, 155, 156], following which the SOC is referred with the SOC-OCV table. These methods permit simultaneous estimation in one recursive framework. As discussed in ref. [83], however, the mapping from OCV to SOC is an open-loop way thus the accuracy is limited, especially if the battery chemistry exhibits a flat SOC-OCV curve. Additionally, the algorithm may suffer from instability or even divergence when the battery model is not accurate enough [90]. As for the second category, the model identification and SOC estimation are carried out dually with different filters. Typically, the dual estimation method uses two cooperating filters where one estimates the battery state and the other estimates the model parameters. These two filters are separate and work concurrently in parallel with the information exchange. The authors in refs. [126, 129, 151, 157] used RLS to update the model parameters and EKF and its variants to estimate the battery state. These methods are theoretically more accurate than the first category as the SOC is observed in a completely close-loop way. It has to be noted that two common drawbacks exist concerning either of the two categories of methods. Firstly, the cross interference

between model identification and state estimate may compromise the numerical stability and accuracy of algorithm substantially, i.e. the uncertainty on SOC estimate disturbs the model identification and vice versa [158]. Secondly, the battery capacity as another crucial parameter to influence the SOC estimation has not been identified.

The capacity is a figure of merit describing the SOH of battery. Timely capacity adaption further facilitates SOC estimation as the capacity is involved in the state equation of most ECM based SOC observers. The model-based close-loop methods augment the ECM to include the battery capacity in the form of either a model parameter or a system state [90]. The existing methods for capacity estimate have been reviewed detailed in Section 2.4.4. Lee et al. [120] estimated the SOC and capacity dually with the DEKF. However, the non-adaption of model parameters may lower down the accuracy when the working condition changes or the battery degrades. Hua et al. [121] applied the DNPf for lithium-ion batteries. However, only the ohmic resistance was updated and the other model parameters were left without adaption. In refs [94, 95], the capacity was treated as a model parameter, then the full set of model parameters and SOC were estimated concurrently with the DEKF. The adaption of all relevant model parameters enhances the robustness of these methods to the operating condition variation and battery degradation. However, the high-order EKF for parameters identification may be subject to instability issues [42], especially when it is running in parallel with the state estimator with both information exchange and cross interference. The high-dimension matrix operations such as matrix inversion also occupy heavy computational resources thus complicate its implementation on the low-cost microcontrollers. Zou et al. [42] proposed a fourth-order EKF for SOC and capacity joint estimation. The model parameters including the ohmic resistance and battery capacity were updated periodically in a macro timescale. Again, the computational complexity and numerical stability remains as a problem and the algorithm has to be operated offline to guarantee the stability.

In this chapter, the SOC and capacity are estimated jointly based on an online identified battery model. Unlike the existing approaches, the OCV dynamics is

separated from the rest of dynamics for the model characterization. The RLS based model identification is designed to be fully decoupled from the EKF based state estimation. Owing to the decoupling, the cross interference which risks degrading estimation accuracy and numerical stability is effectively prohibited. The joint estimator comprises a simple OCV estimator and a state EKF with reduced order. Compared with the commonly used state estimators where the polarization voltages have to be included in the state vector, the proposed joint estimator effectively reduces the filter order, which is beneficial for the enhancement of stability and computational efficiency. It should be mentioned that the proposed method works in a close-loop way which is an improvement of the method proposed in Chapter 4. Experiments are carried out to show the fidelity and robustness of the proposed method. Comparison with other popular methods further demonstrates the superiority of the proposed method in terms of convergence speed, estimation accuracy, and computational cost.

The rest of the chapter is organized as follows. Section 5.2 details the battery model and the associated online model identification method. Section 5.3 introduces the SOC and capacity joint estimator and the overall framework of the proposed method. Section 5.4 presents the experimental details. The algorithm verification, comparison, and robustness analysis are conducted in Section 5.5. The conclusions are drawn in Section 5.6.

5.2 Battery Model and Identification

5.2.1 Battery Modeling

Generally, the battery state estimate tends to be more accurate with models that better reproduce the battery dynamics, but at the expense of higher complexity and numerical instability. In this chapter, the first-order RC model as shown in Figure 3.1 is adopted.

5.2.2 Online Model Identification

The electrical behavior of the first-order RC model has already been derived as Eq. (3.1) and Eq. (3.2). In Chapter 4, the ohmic resistance (R_s) and polarization impedances (R_p and C_p) are identified with different estimators. In this chapter, instead, we try to lump them into one parameter vector for joint estimate. The evolution of polarization voltage is expressed by:

$$V_p(t) = e^{-\frac{\Delta t_c}{R_p C_p}} V_p(t - \Delta t_c) + (1 - e^{-\frac{\Delta t_c}{R_p C_p}}) R_p I_L(t - \Delta t_c) \quad (5.1)$$

where Δt_c is the time interval used to identify the model parameters. By substituting Eq. (3.2) into Eq. (5.1), the terminal voltage is expressed as:

$$V_t(t) = V_{oc}(t) - \alpha_1 V_{oc}(t - \Delta t_c) + \alpha_1 V_t(t - \Delta t_c) + \alpha_2 I_L(t) + \alpha_3 I_L(t - \Delta t_c) \quad (5.2)$$

where

$$[\alpha_1 \quad \alpha_2 \quad \alpha_3] = \left[e^{-\frac{\Delta t_c}{R_p C_p}} \quad -R_s \quad R_s e^{-\frac{\Delta t_c}{R_p C_p}} - (1 - e^{-\frac{\Delta t_c}{R_p C_p}}) R_p \right] \quad (5.3)$$

By shifting Eq. (5.2) to the previous time step, the following expression can be drawn:

$$V_t(t - \Delta t_c) = V_{oc}(t - \Delta t_c) - \alpha_1 V_{oc}(t - 2\Delta t_c) + \alpha_1 V_t(t - 2\Delta t_c) + \alpha_2 I_L(t - \Delta t_c) + \alpha_3 I_L(t - 2\Delta t_c) \quad (5.4)$$

Subtracting Eq. (5.4) from Eq. (5.2) yields:

$$\Delta V_t(t) = \Delta [V_{oc}(t) - \alpha_1 V_{oc}(t - \Delta t_c)] + \alpha_1 \Delta V_t(t - \Delta t_c) + \alpha_2 \Delta I_L(t) + \alpha_3 \Delta I_L(t - \Delta t_c) \quad (5.5)$$

where $\Delta V_t(t)$ is defined as the differential voltage $V_t(t) - V_t(t - \Delta t_c)$, and the analogous definition applies to the other terms. Within this context, Eq. (5.5) can be expressed in the regression form as:

$$\Delta V_t(t) = \phi^T(t)u(t) + e_1(t) \quad (5.6)$$

where

$$\begin{aligned} \phi(t) &= [\alpha_1 \quad \alpha_2 \quad \alpha_3]^T \\ u(t) &= [\Delta V_t(t - \Delta t_c) \quad \Delta I_L(t) \quad \Delta I_L(t - \Delta t_c)]^T \\ e_1(t) &= \Delta[V_{oc}(t) - \alpha_1 V_{oc}(t - \Delta t_c)] \end{aligned} \quad (5.7)$$

Considering the slow varying OCV of the VRB, it can be validated that the error term $e_1(t)$ is subtle and even negligible within a sufficiently small Δt_c . The regression model represented by Eq. (5.6) is solved with RLS which is widely implemented in real applications for the low computational cost. A user-defined forgetting factor λ is employed in order to emphasize the significance of the most recently obtained data and give less weight to the old data. The algorithmic procedures of RLS is not detailed here but can be referred to ref. [143]. After the regression model is solved, the model parameters can be reversely deducted as:

$$\begin{bmatrix} R_s & R_p & C_p \end{bmatrix} = \begin{bmatrix} -\alpha_2 & \frac{\alpha_1 \alpha_2 + \alpha_3}{\alpha_1 - 1} & \frac{(1 - \alpha_1) \Delta t_c}{(\alpha_1 \alpha_2 + \alpha_3) \ln \alpha_1} \end{bmatrix} \quad (5.8)$$

5.3 Joint Estimation of SOC and Capacity

5.3.1 A Simple OCV Estimator

The conventional state estimator [42, 159, 160] integrates the polarization voltage (V_p), SOC, and any other states of interest into one vector as the system state and applies the terminal voltage as system measurement. It is known that the high-order filter is computational heavy as a consequence of high dimension of matrix operation. Moreover, the high-order filter suffers from instability issues more easily [42]. To address this problem, this section goes further to derive a joint estimator with reduced order. To achieve this, a very simple OCV estimator introduced in Section 4.2 is used also for this chapter. However, the derivation in Section 4.2 is

only applicable to the simplest first-order RC model. In this section, we derive a more general framework of such OCV estimator which can be easily generalized to higher-order RC models.

The OCV is observed with the aid of battery model characterization. Converting Eq. (5.1) to the frequency domain yields:

$$V_p(z^{-1}) = e^{-\frac{t_s}{R_p C_p}} z^{-1} V_p(z^{-1}) + (1 - e^{-\frac{t_s}{R_p C_p}}) R_p z^{-1} I_L(z^{-1}) \quad (5.9)$$

By defining $\beta = \exp(-t_s / R_p / C_p)$, V_p can be solved in the z -domain as:

$$V_p(z^{-1}) = \frac{(1 - \beta) R_p z^{-1}}{1 - \beta z^{-1}} I_L(z^{-1}) \quad (5.10)$$

According to the relationship of Eq. (3.2), the following expression can be drawn:

$$V_{oc}(z^{-1}) = V_t(z^{-1}) + \left[\frac{(1 - \beta) R_p z^{-1}}{1 - \beta z^{-1}} + R_s \right] I_L(z^{-1}) \quad (5.11)$$

Eq. (5.11) can be reversed to the discrete-time domain as:

$$\begin{aligned} V_{oc}(k) = & \beta V_{oc}(k-1) + V_t(k) - \beta V_t(k-1) \\ & + R_s I_L(k) + [(1 - \beta) R_p - \beta R_s] I_L(k-1) \end{aligned} \quad (5.12)$$

where k is the time index. By applying transposition to Eq. (5.12), the OCV can be solved as:

$$V_{oc}(k) = \hat{V}_{oc}(k) + e_2(k) \quad (5.13)$$

where

$$\begin{aligned} \hat{V}_{oc}(k) = & \frac{[V_t(k) - \beta V_t(k-1) + R_s I_L(k) + (R_p - \beta R_p - \beta R_s) I_L(k-1)]}{1 - \beta} \\ e_2(k) = & \beta [V_{oc}(k-1) - V_{oc}(k)] / (1 - \beta) \end{aligned} \quad (5.14)$$

The error term, represented by $e_2(k)$, becomes sufficiently small and ignorable by assuming a slowly varying OCV within a short time interval, which is aligned with the nature of the VRB and most other battery chemistries. Therefore, $\hat{V}_{oc}(k)$ can be treated as the estimate of OCV. It has to be noted that the OCV estimator described by Eqs. (5.9) - (5.14) is a generic framework and is easily extended to the version of the N -th order RC model. Specifically, the derivation of the simple OCV estimator on the second-order RC model which is also widely implemented in open literatures is illustrated in Appendix A.

5.3.2 EKF-based Joint Estimation

The SOC can be directly inversed from $\hat{V}_{oc}(t)$ with the SOC-OCV look-up table, as adopted by the method discussed in Chapter 4 [140]. This approach, however, is expected to be further improved especially for the battery chemistries exhibiting a very flat SOC-OCV correlation which is not easily invertible. For the VRB of interest, the OCV drops at a rate of 1.65 mV per unit of SOC when the battery is operated between 30% and 70% SOC, indicating that a small estimation error on OCV can lead to a sufficient SOC error. This will be further verified from the experimental result in Section 5.5.1. To address this problem, an EKF based state estimator applying $\hat{V}_{oc}(t)$ as the noisy system measurement is formulated here to estimate the SOC and capacity jointly.

The SOC recurrent relationship is expressed as:

$$s_{k+1} = s_k - \frac{\eta I_L(k) t_s}{Q_k} \quad (5.15)$$

As the polarization voltage (V_p) has no correlation with OCV, it has no need to be included in the state vector. In this way, the filter order can be compressed compared with the conventional state estimator. In this chapter, the state vector is defined as $x = [s \ 1/Q]^T$ and $\hat{V}_{oc}$ is treated as the noisy measurement. Under such definition, the state space function is expressed as:

$$\begin{aligned} x_{k+1} &= F(x_k) + w_k = \begin{bmatrix} 1 & -\eta t_s I_L(k) \\ 0 & 1 \end{bmatrix} x_k + w_k \\ \hat{V}_{oc,k} &= G(x_k) + v_k \end{aligned} \quad (5.16)$$

where w_k is the process noise, v_k is the estimation error of the simple OCV estimator which is treated as the measurement noise here. $G(x_k)$ is the relation of state vector and battery OCV. The expression of $G(x_k)$ is determined with the SOC-OCV test. The detailed description of EKF can be found in ref [144], while the algorithmic procedures are summarized in Figure 5.1.

Figure 5.1 Algorithmic Procedure of EKF for the joint estimation

The relevant matrices $\hat{A}_k$ and $\hat{C}_k$ are updated at each iteration as:

$$\hat{A}_k = \frac{\partial F(x_k)}{\partial x_k} \bigg|_{x_k = \hat{x}_k^+} = \begin{bmatrix} 1 & -t_s I_L(k) \\ 0 & 1 \end{bmatrix} \quad (5.17)$$

$$\hat{C}_k = \frac{\partial G(x_k)}{\partial x_k} \bigg|_{x_k = \hat{x}_k^-} = \begin{bmatrix} \frac{dV_{oc}}{ds} \bigg|_{s_k = \hat{s}_k^-} & 0 \end{bmatrix} \quad (5.18)$$

The second entry of $\hat{C}_k$, i.e. $dV_{oc}/d(1/Q)$, is approximately zero because the SOC-OCV correlation of VRB is not sensitive to the capacity decay, as discussed in Chapter 4. The proposed joint estimator reduces the filter order thus shows the merits of lower computational cost and higher numerical stability. It should be noted that the order reduction brought by the proposed joint estimator will be much more significant if higher-order RC models are used. Specifically, the order can be reduced by N if an N th-order RC model is applied as all the polarization voltages can be omitted from the state vector.

5.3.3 Algorithm Framework

In this chapter, the model identification and the SOC/capacity joint estimation are executed in a fully decoupled way. The computational efficient RLS is adopted to online adapt the model parameters, which are further injected into the joint estimator for enhanced SOC and capacity estimation. The SOC and capacity joint estimator consists of two parts. The first part is a very simple OCV estimator based on Eq. (5.14). The estimated OCV is treated as the noisy system measurement of the state estimator represented by Eq. (5.16), which constitutes the second part of the joint estimator. Except for outputting SOC and instantaneous capacity, an auxiliary function of the proposed method is to predict the battery terminal voltage for the next onboard sampling time, which is essential for many energy management issues such as peak power determination [136]. The implementation flowchart of the proposed method is shown in Figure 5.2.

$$V_{oc}(s) = \sum_{i=0}^{n_p} c_i s^i \quad (5.19)$$

where c_i is the coefficient; and n_p is the order of polynomial fitting and is equal to 5 in this chapter. The polynomial coefficients are extracted with the LS method. The calibrated SOC-OCV curve is shown in Figure 5.3 (a). It should be noted that the SOC-OCV correlation is theoretically affected by the working temperature of VRB. However, the VRB should be operated within the temperature range of 10°C to 40°C in order to prevent the thermal precipitation of the vanadium species. Within the narrow temperature range, the SOC-OCV variation caused by temperature is very limited especially for the SOC range of 10% to 90% which is the typical operation range of VRB. The temperature effect has been evaluated and the results suggest that the OCV deviation from the case of 22°C is up to about 10 mV for the above mentioned temperature range. The average deviation is only about 5 mV which is equal to the measurement error limits of sensors in the battery cycler. Therefore, the temperature effect is ignored and the OCV is not treated as the function of temperature to ease the calculation. It should be noted the temperature effect cannot be ignored for the power batteries like lithium-ion as the working temperature range of them are quite wide. Usually the OCV should be considered as a binary function of both temperature and SOC.

5.4.3 Hybrid Pulse Experiments

Two hybrid pulse experiments, named as HPE1 and HPE2, are performed to judge the effectiveness and robustness of the proposed method. A user-defined hybrid pulse current profile is loaded to excite the battery. The measured load current, terminal voltage and the recorded SOC reference of HPE1 are shown in Figure 5.3 (b). For the purpose of algorithm verification, the proposed method is applied on the measured current and voltage data with random initialization on model parameters, SOC, and capacity. The estimated SOC and capacity are then compared with their reference values for evaluation.

Figure 5.3 Battery tests: (a) SOC-OCV curve; (b) profile of current, terminal voltage, and reference SOC for HPE1

The HPE2 is conducted in the same manner but under different conditions. The battery is fully charged and discharged for several days after HPE1, during which period the capacity fading occurs and a new aging state is reached. Following that, HPE2 is carried out under a different operating flow rate to evaluate the robustness of the proposed method against battery degradation and operating conditions variation. The detailed information about the two experiments is summarized in Table 5.1.

Table 5.1 Details of the two hybrid pulse experiments

	Capacity	Flow rate	Temperature	Current
HPE1	2994.5 mAh	120 mL min ⁻¹	22±1°C	Figure 5.3 (b)
HPE2	2585.1 mAh	80 mL min ⁻¹	22±1°C	Figure 5.3 (b)

5.5 Verification and Discussion

In this section, the proposed method is applied on the experimental data of HPE1 and HPE2 to evaluate its fidelity. To test the robustness of the proposed method against uncertain initialization, the algorithm is erroneously initialized as follows throughout this chapter if not otherwise stated:

$$R_s = R_p = 10 \text{ m}\Omega, C_p = 1 \text{ kF}, \text{SOC}_0 = 50\%, Q_0 = 4 \text{ Ah}.$$

5.5.1 OCV Estimation

The experimental data from HPE1 are used and the OCV estimate results are shown in the top plot of Figure 5.4. As shown, the simple OCV estimator approaches the reference trajectory rapidly and tracks the change of OCV with an acceptable mean error of 3.6 mV. As a straightforward way, the SOC can be inferred directly according to the SOC-OCV look-up table, as shown in the middle and bottom plot of Figure 5.4. Unfortunately, the estimated SOC is seen to fluctuate heavily within the $\pm 5\%$ error bound for most of the time. Additionally, couples of large error spikes up to 18.1% are observed, which is obviously undesirable as the sudden jump or drop of SOC will confuse the users' judgment on the remaining energy. The large SOC error is mostly due to the small slope of the SOC-OCV curve as the estimation error on OCV, albeit small, may lead to sufficiently large errors on SOC under this condition. From the results, we conclude that although the simple OCV estimator can provide approximate estimate on OCV, the direct mapping to SOC is not adequate. In this chapter, the EKF based state estimator is added with the expectation to achieve more reliable SOC estimate.

Figure 5.4 Estimation result of OCV and SOC with the simple OCV estimator

5.5.2 Necessity of Updating Model Parameters

To verify the necessity of online model adaption, the proposed algorithm and the non-updating EKF with fixed model parameters are both executed on the experimental data from HPE1 to evaluate the performance. The comparison results are shown in Figure 5.5. By the proposed method, it is observed that both the estimated SOC and capacity converge to the reference value stably and accurately even with large initialization errors. A transitory overshoot occurs for the SOC at the start-up stage when the algorithm tries to correct the large initialization error. However, the overshoot dies out quickly and the estimated SOC matches the reference trajectory with quite high precision as time evolves. With respect to the convergence of SOC, the estimated capacity converges much slower. However, the

slow convergence is acceptable as the capacity varies quite slowly with a very large timescale. In summary, the proposed method proves to be highly authentic for online applications considering the high accuracy and good robustness to uncertain initialization.

Figure 5.5 SOC and capacity estimation result with the proposed method and the non-updating EKF

By comparison, the non-updating EKF demonstrates a decline of accuracy as a consequence of lacking model adaption. Although the estimated SOC converges to the reference value easily, the estimation error is much larger. The estimated capacity also shows a slow damping near the reference due to the poorly estimated SOC. From the comparison, it is evident the proposed method remarkably improves the accuracy without compromising the convergence speed. Moreover, although the

SOC error by non-updating EKF is acceptable (within 3% error bound) for the present case, the estimation will be quite deteriorated when the battery ages gradually or the operating conditions change, as the non-adaption mechanism cannot compensate for the model uncertainty caused by these factors. The capacity estimation will also degrade as a consequence of the deteriorated SOC estimate.

5.5.3 SOC and Capacity Joint Estimation

To assess the performance of the proposed method, the RLS-EKF [129, 151, 157] as one of the state-of-the-art techniques in model parameter and state co-estimation is also executed to compare the results. The RLS-EKF is chosen here as it is more accurate than the non-updating EKF due to the online model adaption, while it is more stable and occupies much less computational resources than the DEKF. Unlike the proposed method, the RLS-EKF has to include the polarization voltages into the state vector. To realize simultaneous estimation, the state vector of RLS-EKF is formulated as $[V_p \ s \ 1/Q]^T$, while the system measurement is the onboard measured V_t . The result of model identification by both of the two methods is shown in Figure 5.6. It should be noted that the forgetting factor of the RLS-based model identification is 0.995 in this chapter. The reference values of model parameters should be calibrated to evaluate the proposed method for model identification. To achieve this, a few discretized time points are selected during the hybrid pulse experiment at a certain time interval. A batch of current and voltage data are sampled to form a data set around each time point and the model parameters are extracted offline by the following procedures:

- (1) The reference V_{oc} is obtained with Eq. (5.19).
- (2) The ohmic resistance (R_s) is determined by the instantaneous voltage variation following a step change of current, i.e. $R_s = \Delta V_t / \Delta I_L$.
- (3) After V_{oc} and R_s are extracted, V_p is obtained with Eq. (3.2). Then R_p and C_p are extracted by solving the below regression model:

$$V_p(k) = [V_p(k-1) \ I_L(k-1)] \phi(k) \quad (5.20)$$

where $\phi(k)$, expressed by $[e^{-t_s/(R_p C_p)} \quad (1 - e^{-t_s/(R_p C_p)}) R_p]^T$, is the parameter vector to be identified. A batch of data is sampled and $\phi(k)$ is determined with the LS method.

Figure 5.6 Comparison results with the proposed method and the RLS-EKF for online model identification under HPE1

It is observed from Figure 5.6 that all the three model parameters exhibit time-varying and SOC-dependent properties, which serves as another strong proof for the need of online model identification. In terms of online identification results, the erroneously initialized model parameters converge to their reference values gradually and keep on tracking them over the entire experiment with both the two methods. As a result, the time-consuming and error-prone calibration of battery model can be avoided. The proposed method converges much faster with a smaller

steady state error than the RLS-EKF. The improvement is supposed to be brought by the cross interference elimination as a result of decoupling the model identification and state estimate. By comparison, the RLS-EKF updates the SOC and model parameters in a coupled method with information exchange at each iteration. The existence of cross interference is seen to deteriorate the stability and accuracy to some extent.

The results of SOC and capacity joint estimate are shown in Figure 5.7. As observed, the proposed method projects the trajectory of SOC accurately with fast convergence from the initial offset. By comparison, the RLS-EKF generates larger errors at the start-up stage, which is supposed to be caused by two reasons: (1) The cross interference between model identification and state estimation may decline the stability and accuracy of them both especially at the initial stage. This can also be supported by the slower convergence of model parameters by using RLS-EKF as shown in Figure 5.6. (2) The stability of higher-order EKF is theoretically lower than the proposed EKF with reduced order. The estimated capacity also converges gradually to the calibrated trajectory with either of the two algorithms. By comparison, the proposed method converges faster with less deviation at the initial stage, mostly due to the better SOC estimation result.

The convergence time and the estimation error after convergence are used as a performance measure to evaluate the two algorithms quantitatively. The convergence time is defined as the time when the estimated SOC/capacity starts to be stable within the 5%/10% error bound. The MAE, RMSE, and convergence time are summarized in Table 5.2. The results suggest that the proposed method outperforms the RLS-EKF in terms of both convergence speed and estimation accuracy.

Figure 5.7 Comparison result with the proposed method and the RLS-EKF for SOC and capacity joint estimation under HPE1

Table 5.2 Performance comparison of the proposed method and RLS-EKF for HPE1

	SOC estimation		Capacity estimation	
	RLS-EKF	Proposed method	RLS-EKF	Proposed method
MAE	1.08%	0.56%	3.12%	2.47%
RMSE	1.28%	0.69%	3.56%	3.06%
Convergence time	57 s	64 s	3487 s	2244 s

5.5.4 Robustness Analysis against Aging and Operating Condition Variation

Both the two methods are applied on the experimental data of HPE2 to test their

robustness to battery aging and operating conditions variation. The estimation results are plotted in Figure 5.8. In accordance with the results of HPE1, the proposed method generates smaller error compared with the RLS-EKF especially at the start-up stage. The MAE, RMSE, and convergence time are listed in Table 5.3. The proposed method shows faster convergence and smaller estimation error, which clearly indicates its superiority to the RLS-EKF. The high accuracy and fast convergence also verify the robustness of the proposed method against battery aging and operating condition variation.

Figure 5.8 Comparison of the SOC and capacity joint estimation based on the proposed method and the RLS-EKF for HPE2

It should be noted that the proposed methods in this chapter and throughout the thesis do not incorporate the aging model which is based on the complicated PDEs.

However, a capacity fade from 2994.5 mAh (HPE 1) to 2585.1 mAh (HPE 2) has represented a substantial aging of 13.67% and we have shown that the robustness is satisfactory for such a degree of aging. However, whether the proposed method can perform well when the battery has reached the end of life is still doubtful based on the results presented in this thesis. In order to fully address this problem, it is recommended that the SOC-OCV correlation should be recalibrated every time when the VRB drops 10% in the total capacity. This is applicable because a capacity fade of 10% is a significant aging in commercial VRB systems and will costs a long time to arrive. This is also implementable from the technical perspective as the online capacity estimation method has already been investigated and verified in this chapter.

Table 5.3 Performance comparison of the proposed method and RLS-EKF for HPE2

	SOC estimation		Capacity estimation	
	RLS-EKF	Proposed method	RLS-EKF	Proposed method
MAE	1.27%	0.59%	1.95%	1.57%
RMSE	1.32%	0.67%	2.70%	2.31%
Convergence time	55 s	63 s	2466 s	424 s

5.5.5 Computational Cost

As computational burden is an indispensable concern in real applications, it is worthwhile to investigate the time consumption of the proposed method in comparison with other mature methods. For comparison purposes, the non-updating EKF and the RLS-EKF are also discussed in this section. The algorithms are executed repeatedly on the data of HPE1 for 10 times to calculate the average CPU time for each iteration in order to quantify the computational cost. The comparative result is shown in Table 5.4. The proposed method is seen to improve the computational speed by 25.6% while enhances the estimation performance at the same time compared with the RLS-EKF. The reduction of CPU time comes from the fact that the proposed joint estimator lowers down the filter order thus reduces the dimension of matrix operation. Compared with the non-updating EKF which

represents the simplest close-loop state estimation framework, the proposed method adds the function of online model parameters adaption but consumes only slightly more CPU time at about 5.3%. It has to be noted that the computational cost reduction discussed here represents the most modest situation, as the filter order only reduces by 1 when the simplest first-order RC model is applied. However, if higher-order RC models are adopted, the computational efficiency will be improved much more as all the polarization voltages will be removed from the state vector. The comparison of both estimation performance and computational cost explicitly shows the superiority of the proposed method.

Table 5.4 CPU time of the three algorithms

	Non-updating EKF	RLS-EKF	Proposed method
CPU time	75.823 μ s	107.326 μ s	79.857 μ s

5.6 Conclusions

The model parameters and battery states are mostly estimated in an integrated way in the existing studies. These integrated methods may suffer from cross interference resulting in reduction of numerical stability and accuracy. In this chapter, we propose a fully decoupled approach, where the RLS based model adaption and the EKF based state estimation are operated independently to eliminate the cross interference. A novel SOC and capacity joint estimator is proposed to effectively lower down the filter order so that both stability and computational efficiency are improved. Experimental results suggest that the model is accurately updated with the proposed method so that the time-consuming calibration is avoidable. The SOC and capacity are estimated in real time with fast convergence and high accuracy. The comparison with other popular methods further highlights the superiority of the proposed method in terms of accuracy, convergence speed, and computational cost. Additionally, the proposed method also proves to be robust against the operating condition variation and its robustness to aging is satisfactory within an aging degree of 13.67%.

CHAPTER 6 Enhanced Online Model Identification and Stage of Charge Estimation with a FBCRLS Based Observer for Noise Attenuation

6.1 Introduction

Online model identification is of great importance to not only SOC estimate but also some other battery management issues like system diagnosis and efficiency enhancement. The existing methods for model parameters and SOC co-estimate as well as their advantages and disadvantages have been reviewed in Section 5.1. The existing methods provide satisfactory results when only the system output noises and state noises are present. However, the battery systems are also subjected to unexpected input noise, which will cause identification bias and degrade the precision of identification inevitably. Even with high resolution sensors for measurement, the noise may still be present due to data acquisition process or analog-to-digital conversion. The bias compensating recursive least squares (BCRLS) method is a candidate to solve this kind of error-in-variables (EIV) problem, but with requirement of the prior knowledge of noise statistics which are quite hard to obtain in real applications. Sitterly et al. [161] corrected the identification bias on battery model parameters in a simulation study by assuming the noise characteristics were known. Liu et al. [162] applied signal averaging to attenuate the noise effect. The signals have to be sampled at a much faster rate than the SOC estimate. The intermediate storage of the large amount of measured data also causes high memory consumption.

In this chapter, concurrent model identification and SOC estimation is explored. The existence of noises is firstly shown to cause bias on model identification. To eliminate the noise effect, a Frisch scheme based bias compensating recursive least squares (FBCRLS) method is constructed to estimate the noise variances and the unbiased model parameters in real time. The FBCRLS is further designed to be integrated with an SOC observer in a close loop feedback mechanism to form a

complete framework, namely FBCRLS based observer. Simulation and experimental results show that the proposed method is highly authentic in both online model adaption and SOC estimate. The comparison with existing methods highlights its superiority in terms of accuracy and convergence speed when additive noises are present. To the best of the authors' knowledge, it has not been investigated elsewhere regarding online noise statistical estimation for enhanced model identification and SOC estimate.

The rest of this chapter is organized as follows. In Section 6.2, the battery modeling, BCRLS based model parameterization, and the SOC observer design are detailed. In Section 6.3, the online noise variance estimation based on the Frisch scheme is introduced, after which the whole framework of the FBCRLS based SOC observer is put forward. Simulation studies are conducted in Section 6.4. In Section 6.5, experiments are carried out on a lab-scale VRB to verify the proposed algorithm. The algorithm is further tested on a lithium-ion battery to verify its robustness against multiple battery chemistries. Section 6.6 concludes this chapter.

6.2 Battery Model Identification and SOC Estimate

In this section, the battery model and the associated model identification method is detailed. Based on the online adapted battery model, an adaptive SOC observer is designed. The model identification and SOC estimate are integrated together in the form of co-estimation.

6.2.1 Battery Modeling

Concerning the trade-off between accuracy and complexity, the first-order RC model as a mature battery model is applied. The structure of first-order RC model is shown in Figure 6.1 (a). The electrical behavior of the used battery model can be expressed by Eq. (3.1) and Eq. (3.2). It is widely known that the relationship between SOC and OCV is intrinsically nonlinear, and the mathematical fitting of it, if possible, will increase the complexity of SOC observer substantially. To address this problem, the SOC-OCV map is decomposed into nine linear segments here, as

shown in Figure 6.1 (b). Each segment is approximated with the below linear equation:

$$V_{oc} = f(s) = c_0 + c_1 s \quad (6.1)$$

where c_0 and c_1 are the polynomial coefficients of each linear segment.

Figure 6.1 First-order RC model: (a) schematic diagram of battery model; (b) SOC-OCV correlation of VRB

6.2.2 Regression Structure of Battery Model

By defining $V_q = V_t - V_{oc}$, the transfer function of the battery system behavior can be expressed as:

$$\frac{V_q(\zeta)}{I_L(\zeta)} = -\frac{R_s + R_p + R_s R_p C_p \zeta}{1 + R_p C_p \zeta} \quad (6.2)$$

where ζ represents the complex number frequency parameter defined under Laplace transform. Throughout this chapter, I_L is treated as system input while V_q is

treated as system output. By applying the bilinear transform $\varsigma = 2(z-1)/t_s/(z+1)$ to Eq. (6.2), we can obtain:

$$\frac{V_q(z^{-1})}{I_L(z^{-1})} = \frac{b_0 + b_1 z^{-1}}{1 + a_1 z^{-1}} \quad (6.3)$$

The related coefficients are calculated by:

$$\begin{cases} a_1 = (1 - 2R_p C_p) / (1 + 2R_p C_p) \\ b_0 = -(R_s + R_p + 2R_s R_p C_p) / (1 + 2R_p C_p) \\ b_1 = -(R_s + R_p - 2R_s R_p C_p) / (1 + 2R_p C_p) \end{cases} \quad (6.4)$$

The frequency-domain system represented by Eq. (6.3) can be reversed to the discrete-time domain as:

$$V_{q,k} = -a_1 V_{q,k-1} + b_0 I_{L,k} + b_1 I_{L,k-1} = \theta_k^T \varphi_k \quad (6.5)$$

where

$$\begin{aligned} \theta &= [a^T \ b^T]^T; a = [a_1]^T; b = [b_0 \ b_1]^T \\ \varphi_k &= [\varphi_{y,k}^T \ \varphi_{u,k}^T]^T; \varphi_{y,k} = [-V_{q,k-1}]^T; \varphi_{u,k} = [I_{L,k} \ I_{L,k-1}]^T \end{aligned} \quad (6.6)$$

It is evident that the system becomes identifiable with the regression model of Eq. (6.5). The RLS method is commonly used to solve the regression model in the existing works.

6.2.3 BCRLS Based Model Identification

In this section, a simulation study is firstly carried out to show that the standard RLS is asymptotically biased, i.e. identification will converge to values away from the true values, when both $V_{t,k}$ and $I_{L,k}$ are corrupted with noises. The battery model shown in Figure 6.1 (a) is built in Matlab Simulink and the model parameters are defined as: $R_s = 60 \text{ m}\Omega$, $R_p = 20 \text{ m}\Omega$, and $C_p = 1.5 \text{ kF}$. The V_{oc} is assumed to be

stable at 1.4 V over the entire simulation. A dynamic current profile is applied and the corresponding terminal voltages are calculated from the battery model. White noises with variances σ_i and σ_v are imposed on the noise-free current and voltage data to evaluate their effects. After that, the standard RLS is executed on the simulated battery data and the identification result is shown in Figure 6.2. As indicated, the identification bias is remarkable in the presence of noise corruption, especially for the identification of R_p and C_p . The results also demonstrate an enlargement of the identification bias as a consequence of increasing noise variance.

Figure 6.2 Standard RLS based model identification with noise corruption

The bias compensating least squares (BCLS) method is a favorable candidate to remove the identification bias caused by additive noises. The BCLS method treats regression system of Eq. (6.5) as a typical EIV system as depicted in Figure 6.3.

Figure 6.3 Schematic diagram of the typical EIV system

The noisy input and output of the linear system are expressed as:

$$\begin{cases} V_{q0,k} = V_{t,k} + \tilde{V}_{t,k} - V_{oc,k} = V_{q,k} + \tilde{V}_{t,k} \\ I_{L0,k} = I_{L,k} + \tilde{I}_{L,k} \end{cases} \quad (6.7)$$

where $\tilde{I}_L$ and $\tilde{V}_t$ are the measurement noises on I_L and V_t , respectively, and the analogous definition applies throughout this chapter if not otherwise stated. In this chapter, the noises $\tilde{I}_L$ and $\tilde{V}_t$ are assumed to be zero-mean white noises with variance σ_i and σ_v , respectively. It is also assumed $\tilde{I}_L$ and $\tilde{V}_t$ are both uncorrelated with their true values and mutually uncorrelated.

In order to describe the BCLS and further the Frisch scheme in a clear way, we first define the auto covariance matrix of arbitrary vector p and the cross covariance matrix of two arbitrary vectors p and q as follows:

$$\begin{aligned} \Gamma_p &= E(pp^T) \\ \Gamma_{pq} &= E(pq^T) \end{aligned} \quad (6.8)$$

where $E(\bullet)$ represents the expected value operator. Similarly, the cross covariance matrix between arbitrary vector p and a stochastic process r is defined as:

$$\chi_{pr} = E(pr) \quad (6.9)$$

According to assumptions on noises, the covariance matrix of the noise-free data vector φ_k is expressed as:

$$\Gamma_{\varphi,k} = \Gamma_{\varphi_0,k} - \Gamma_{\tilde{\varphi},k} \quad (6.10)$$

where $\Gamma_{\tilde{\varphi},k}$ is the noise covariance matrix expressed by $\Gamma_{\tilde{\varphi},k} = \text{diag} \{ \sigma_v, \sigma_i, \sigma_i \}$.

Then the BCLS based identification is expressed as:

$$\theta_k^{BCLS} = \left(\Gamma_{\varphi_0,k} - \Gamma_{\tilde{\varphi},k} \right)^{-1} \chi_{\varphi_0 v_{q0},k} \quad (6.11)$$

As the matrix inversion is computational heavy and not easily implementable, it is plausible to find a recursive way to solve this problem. We apply regular matrix splitting to Eq. (6.11) and the following equation can be drawn:

$$\theta_k^{BCRLS} = \theta_k^{RLS} + \Gamma_{\varphi_0,k}^{-1} \Gamma_{\tilde{\varphi},k} \theta_{k-1}^{BCRLS} \quad (6.12)$$

where θ_k^{RLS} is the result of the standard RLS. Eq. (6.12) constitutes the update law of BCRLS which is easier to implement in real applications. The matrix inversion term $\Gamma_{\varphi_0,k}^{-1}$ can be replaced by the error covariance matrix, which is recursively updated with the standard RLS, to ease the computation.

6.2.4 Design of SOC Observer

Based on the identified model parameters, a SOC observer is designed to estimate SOC as a system state in this section. SOC is defined as the percentage of remaining capacity with respect to the maximum available capacity. The evolvement of SOC with time is expressed by:

$$s(t) = s(t_0) - \frac{1}{Q} \int_{t_0}^t \eta I_L(\tau) d\tau \quad (6.13)$$

By defining the state vector as $x = [V_p \quad s]^T$ and the system output as V_t , the state-space model is formulated as:

$$\begin{cases} \dot{x}(t) = Ax(t) + BI_L(t) \\ V_t(t) = Cx(t) + DI_L(t) + r_0 \end{cases} \quad (6.14)$$

where

$$\begin{aligned} A &= \begin{bmatrix} -1/(R_p C_p) & 0 \\ 0 & 0 \end{bmatrix} \\ B &= \begin{bmatrix} 1/C_p \\ -1/Q \end{bmatrix} \\ C &= \begin{bmatrix} -1 & c_1|_{s_k=\hat{s}_k^-} \end{bmatrix} \\ D &= -R_s \\ r_0 &= c_0|_{s_k=\hat{s}_k^-} \end{aligned} \quad (6.15)$$

The observability of system described by (6.14) has already been verified in literatures and will not be further discussed here. Then the closed-loop state observer can be written as:

$$\begin{cases} \dot{\hat{x}}(t) = A\hat{x}(t) + BI_L(t) + L[V_t(t) - \hat{V}_t(t)] \\ \hat{V}_t(t) = C\hat{x}(t) + DI_L(t) + r_0 \end{cases} \quad (6.16)$$

where L is the feedback gain, which is designed by the pole placement. Assuming the poles of observer are desired to be po_1 and po_2 both of which are negative, the characteristic polynomial can be written as $pn = (g + po_1)(g + po_2) = g^2 + d_1g + d_2$. Various formulas can be used to tune the feedback gain for pole placement. The Ackermann's Formula is adopted here as below:

$$L = (A^2 + d_1A + d_2I) \begin{bmatrix} C \\ CA \end{bmatrix}^{-1} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (6.17)$$

6.3 Frisch Scheme based Noise Statistics Estimation

The BCLS can rule out the identification bias provided that the statistical properties of noises are known. In this section, the noise variances are estimated in real time

by integrating the Frisch scheme into the co-estimation method developed in Section 6.2.

6.3.1 Fundamental of Frisch Scheme

It is validated that Eq. (6.5) can be reformulated as:

$$\bar{\varphi}_k^T \bar{\theta}_k^T = 0 \quad (6.18)$$

where $\bar{\varphi}_k$ and $\bar{\theta}_k$ are the extended counterpart of φ_k and θ_k , and can be expressed as:

$$\begin{aligned} \bar{\theta} &= [\bar{a}^T \ b^T]^T = [1 \ \theta^T]^T \in \mathbb{R}^{n_\theta+1} \\ \bar{\varphi}_k &= [\bar{\varphi}_{y,k}^T \ \bar{\varphi}_{u,k}^T]^T = [-V_{q,k} \ \varphi_k^T]^T \in \mathbb{R}^{n_\theta+1} \end{aligned} \quad (6.19)$$

The noise-free auto covariance matrix $\Gamma_{\bar{\varphi}}$ is singular and positive semi definite with rank n_θ . Due to the existence of noise, however, the rank of $\Gamma_{\bar{\varphi}_0}$ becomes $n_\theta + 1$. In order to extract the true and noise-free part from the noisy signal, the Frisch scheme tries to solve the below problem.

Problem 1: Given a symmetric auto covariance matrix $\Gamma_{\bar{\varphi}_0}$ with signals corrupted by noise, find the diagonal noise covariance matrix $\Gamma_{\tilde{\varphi}_0}$ such that $\Gamma_{\bar{\varphi}} \geq 0$ with the rank of n_θ .

The solution of Problem 1 defines a set of points (σ_i, σ_v) that satisfy the following relationship [163]:

$$\hat{\sigma}_{v,k} = \lambda_{\min}[F_k] \quad (6.20)$$

where

$$F_k = \Gamma_{\bar{\varphi}_{y0,k}} - \Gamma_{\bar{\varphi}_{y0}\varphi_{u0,k}} \left(\Gamma_{\varphi_{u0,k}} - \hat{\sigma}_{i,k} I_{n_b} \right)^{-1} \Gamma_{\varphi_{u0}\bar{\varphi}_{y0,k}} \quad (6.21)$$

In order to yield a unique solution, the Yule-Walker (YW) criterion is adopted in this chapter to form another constraint. An instrument vector is firstly defined as:

$$\delta_{0,k} = [I_{L0,k-2}, \dots, I_{L0,k-1-n_\delta}]^T \in \mathbb{R}^{n_\delta} \quad (6.22)$$

where $n_{\delta_0} \geq n_\theta + 1$. Then the following equation proves to hold:

$$-\chi_{\delta_0 V_{q0},k} + \Gamma_{\delta_0 \varphi_0,k} \theta_k = 0 \quad (6.23)$$

The proof of the equation can be found in Appendix B. Inspired from Eq. (6.23), a cost function is defined here as:

$$Cf_k = \frac{1}{2} \left\| -\chi_{\delta_0 V_{q0},k} + \Gamma_{\delta_0 \varphi_0,k} \hat{\theta}_k \right\|_2^2 \quad (6.24)$$

Then the YW based constraint is formulated by finding the best estimate of $\hat{\sigma}_i$ to minimize the cost function, as follows:

$$\hat{\sigma}_{i,k} = \arg \min_{\sigma_i} Cf_k(\sigma_i) \quad (6.25)$$

The Frisch scheme can hence be summarized as solving Eq. (6.20) and Eq. (6.25).

6.3.2 Noise Variances Update

The determination of voltage (output) noise variance σ_v boils down to finding the smallest eigenvalue of F_k as indicated in Eq. (6.20). The eigenvalue decomposition (EVD) is straightforward and accurate but with high computational complexity. Alternatively, the problem can be addressed by minimizing the below Rayleigh quotient (RQ) as a function of matrix F_k and a vector argument denoted by $\mathcal{G}$:

$$\Re(F_k, \mathcal{G}) = \frac{\mathcal{G}^T F_k \mathcal{G}}{\mathcal{G}^T \mathcal{G}} \quad (6.26)$$

It is known that the RQ comes to its minimum which is equal to the smallest

eigenvalue of F_k , when $\mathcal{g}$ is taken as the eigenvector corresponding to the smallest eigenvalue. In this chapter, the conjugate gradient method is applied to find the smallest RQ. The details are not illustrated here but can be referred to the literatures [164].

The current (input) noise variance σ_i is estimated by solving the minimization problem defined in Eq. (6.25). General methods involve the line search, conjugate-gradient search, Newton's method, gradient-descent search and evolutionary algorithms. To allow real-time implementation, the gradient-descent method is adopted as follows:

$$\hat{\sigma}_{i,k} = \hat{\sigma}_{i,k-1} - \mu C f_k' \quad (6.27)$$

where μ denotes the step-size parameter. The derivative term can be calculated as:

$$C f_k' = \left. \frac{dC f_k}{d\hat{\sigma}_{i,k}} \right|_{\rho=\hat{\rho}_k} = \frac{dC f_k}{d\theta_k} \left(\frac{\partial \theta_k}{\partial \hat{\sigma}_{v,k}} \frac{d\hat{\sigma}_{v,k}}{d\hat{\sigma}_{i,k}} + \frac{\partial \theta_k}{\partial \hat{\sigma}_{i,k}} \right) \bigg|_{\rho=\hat{\rho}_k} \quad (6.28)$$

where $\rho = [\theta^T \quad \sigma_v \quad \sigma_i]^T$. In order to obtain the derivative terms in Eq. (6.28), the first-order Taylor series approximation of Eq. (6.11) and Eq. (6.20) around the latest estimate $\hat{\rho}_{k-1}$ is written as:

$$\begin{aligned} \hat{\theta}_k &= \hat{\theta}_{k-1} + \left(\Gamma_{\varphi_0,k} - \hat{\Gamma}_{\hat{\varphi},k-1} \right)^{-1} \left(\chi_{\varphi_0 V_{\varphi_0,k}} - \Gamma_{\varphi_0,k} \hat{\theta}_{k-1} + \begin{bmatrix} \sigma_{v,k} \hat{a}_{k-1} \\ \sigma_{i,k} \hat{b}_{k-1} \end{bmatrix} \right) \\ \hat{\sigma}_{v,k} &= \hat{\sigma}_{v,k-1} + \frac{\hat{b}_{k-1}^T \hat{b}_{k-1}}{\hat{a}_{k-1}^T \hat{a}_{k-1}} (\hat{\sigma}_{i,k-1} - \hat{\sigma}_{i,k}) \end{aligned} \quad (6.29)$$

Based on the linearized form of Eq. (6.29), the following equations can be derived:

$$\begin{aligned}
 \frac{dCf_k}{d\theta_k} &= \left(\hat{\theta}_{k-1}^T \Gamma_{\delta_0 \varphi_{0,k}}^T - \chi_{\delta_0 V_{q0,k}}^T \right) \Gamma_{\delta_0 \varphi_{0,k}} \\
 \frac{d\hat{\sigma}_{v,k}}{d\hat{\sigma}_{i,k}} &= \frac{\hat{b}_{k-1}^T \hat{b}_{k-1}}{\hat{a}_{k-1}^T \hat{a}_{k-1}} \\
 \frac{\partial \theta_k}{\partial \hat{\sigma}_{v,k}} &= \left(\Gamma_{\varphi_{0,k}} - \hat{\Gamma}_{\tilde{\varphi},k-1} \right)^{-1} \begin{bmatrix} \hat{a}_{k-1} \\ 0 \end{bmatrix} \\
 \frac{\partial \theta_k}{\partial \hat{\sigma}_{i,k}} &= \left(\Gamma_{\varphi_{0,k}} - \hat{\Gamma}_{\tilde{\varphi},k-1} \right)^{-1} \begin{bmatrix} 0 \\ \hat{b}_{k-1} \end{bmatrix}
 \end{aligned} \tag{6.30}$$

Analogously, the terms with matrix inversion can be solved recursively with the regular matrix splitting.

6.3.3 Algorithm Summary

This chapter proposes a FBCRLS based observer for integrated model identification and SOC estimate. The FBCRLS is used to online adapt the model parameters, which are further injected into the state observer for enhanced SOC estimate. A general diagram of the proposed method is shown as Fig. 3. The auto and cross covariance matrices, used frequently by the FBCRLS, are recursively updated at each iteration by adding the presently obtained data to that from the previous iteration. A user-defined forgetting factor (λ) is applied to emphasize the significance of the most recently obtained data compared with the old data. The principle of covariance matrix propagation is expressed as:

$$\begin{aligned}
 \Gamma_{p,k} &= (1 - 1/\gamma_k) \Gamma_{p,k-1} + p_k p_k^T / \gamma_k \\
 \Gamma_{pq,k} &= (1 - 1/\gamma_k) \Gamma_{pq,k-1} + p_k q_k^T / \gamma_k \\
 \chi_{pr,k} &= (1 - 1/\gamma_k) \chi_{pr,k-1} + p_k r_k / \gamma_k
 \end{aligned} \tag{6.31}$$

where $\gamma_k = \sum_{i=1}^k \lambda^{k-i} = (1 - \lambda^k) / (1 - \lambda)$. The derivation of Eq. (6.31) can be found in

Appendix C as supportive information.

Figure 6.4 General diagram of the proposed FBCRLS based observer

6.4 Simulation Study

A simulation is carried out in Section 6.2.3 to prove the existence of identification bias under noise contamination from the theoretical perspective. It should be noted that the OCV is assumed to be known for that case. In practical applications, however, the OCV has to be online estimated from the observed SOC thus will increase the uncertainty of both model identification and state estimation. To better evaluate the feasibility of the proposed FBCRLS based observer, accordingly, a new simulation study is conducted in this section. The OCV is treated as an unknown variable in this case which better meets the real situation.

6.4.1 Data Acquisition

The battery model shown in Figure 6.1 (a) was built in Matlab Simulink environment. The system is sampled at an interval of 1 s. It is assumed the ohmic and polarization resistances are time-varying while the polarization capacitance is constant over the entire simulation. The noise-free load current and the corresponding terminal voltage obtained from the battery model are shown in Figure 6.5. In order to simulate the actual measured signals with non-ideal sensors,

white noises with variance $\sigma_i = 1 \text{ mA}^2$ and $\sigma_v = 1 \text{ mV}^2$ are imposed on the noise-free current and voltage profiles.

Figure 6.5 Noise-free current profile for the simulation study

6.4.2 Simulation Result and Discussion

By applying the proposed method to the simulated battery data, the model parameters and SOC can be estimated concurrently. To better assess the performance, the FBCRLS based observer is compared with the RLS-EKF [129, 140, 165, 166], which is one of the state-of-the-art methods regarding model parameters and SOC co-estimation. The RLS-EKF method consists of a RLS based model parameter estimator in parallel with an EKF based SOC estimator with necessary information exchange between them. As no prior knowledge on model parameters and SOC is available before the experiment, the two algorithms are erroneously initialized as follows throughout this chapter if not otherwise stated: $R_s = R_p = 10 \text{ m}\Omega$, $C_p = 0.5 \text{ kF}$, and $\text{SOC}_0 = 60\%$. The forgetting factor is 0.985 for both

the simulation study and the experimental study in this chapter.

The comparison results are shown in Figure 6.6. In terms of the RLS-EKF, although the identification of R_s is accurate, the algorithm yields persistent bias on R_p and C_p , which is caused by the noise contamination on both current and voltage signals. In other words, the robustness of RLS-EKF to noise is weak. By comparison, the FBCRLS based observer has the merit of online noise variances estimate thus the bias can be compensated effectively. As shown in Figure 6.7, the estimated variances quickly converge to the true values from the incorrect initialization and keep on tracking them over the entire simulation. The estimated variances, albeit oscillate around their steady-state values, are constrained within a reasonable error bound. Owing to the mechanism of online variances estimate and bias compensation, the proposed algorithm is able to follow the changes in model parameters more accurately after a short transition time for initialization error correction. To quantitatively evaluate the identification enhancement brought by noise compensation, the normalized error vector is defined here as:

$$e_k = \begin{bmatrix} \frac{\hat{R}_{s,k} - R_{s,k}}{R_{s,k}} & \frac{\hat{R}_{p,k} - R_{p,k}}{R_{p,k}} & \frac{\hat{C}_{p,k} - C_{p,k}}{C_{p,k}} \end{bmatrix}^T \quad (6.32)$$

where $\hat{R}_{s,k}$, $\hat{R}_{p,k}$, and $\hat{C}_{p,k}$ are the estimates of the respective model parameters at the k -th time step. Each term in the vector is normalized as a percentage concerning the different scales of data. The mean square deviation (MSD) for estimate at each time step, i.e. $E[\|e_k\|^2]$, is applied here as the performance measure. As shown in Figure 6.6 (d), the MSDs from the FBCRLS based observer distribute entirely under those from the RLS-EKF. For the present simulation, the proposed method yields an average reduction of 43.8 dB on MSD over the RLS-EKF, indicating a quite improved robustness against noise corruption.

Figure 6.6 Identification results of model parameters for the simulation study: (a) R_s ; (b) R_p ; (c) C_p ; (4) MSD

Figure 6.7 Results of noise variance estimation for the simulation study

Based on the updated battery model, the SOC is concurrently estimated and the results are plotted in Figure 6.8. The proposed method, within our expectation,

demonstrates an enhancement of SOC estimate as a consequence of the unbiased model parameters identification. Accordingly, the proposed method is verified to show better robustness to noise corruption and outperform the RLS-EKF in terms of both model identification and SOC estimation.

Figure 6.8 SOC estimation result and SOC error for the simulation study

6.5 Experimental Study

The simulation study verifies the proposed method from the theoretical prospective with an ideal battery model. In real applications, however, there exist some model uncertainties like the erroneous fitting of SOC-OCV function and the unmodeled battery dynamics. Therefore, it is worthwhile to execute the proposed algorithm on the experimental data to assess its fidelity in real applications.

6.5.1 Experimental Setup

Experiments are carried out on a lab-scale VRB cell. Details of the experimental

setup have been introduced in Section 3.4.1. The experimental data are collected by the data acquisition system with a sampling time interval of 1 s and stored in the host computer. The current and voltage profiles are shown in Figure 6.9. White noises with variance $\sigma_i = 4 \text{ mA}^2$ and $\sigma_v = 4 \text{ mV}^2$ are manually added to the measured signals to represent the situation of noise corruption.

Figure 6.9 Measured current and voltage profiles for the experimental study on VRB

6.5.2 Experimental Results and Discussion

Both the proposed FBCRLS based observer and the RLS-EKF are implemented on the experimental data to compare their performances. In order to verify the algorithms for online model identification, the reference values of model parameters are firstly prescribed by offline fitting. Specifically, a batch of current and voltage data without noises added are sampled around each time point, then the reference model parameters are extracted by the offline LS fitting. The results of model

identification are shown in Figure 6.10. As shown, all the model parameters exhibit time-varying and SOC-dependent properties, attesting the need of online model adaption. In this respect, the widely applied non-updating SOC observers with fixed model parameters are theoretically less accurate as they cannot adapt to the change of operating condition and battery aging.

Figure 6.10 Identification results of model parameters for the experimental study on VRB

The result shown in Figure 6.10 indicates that the proposed method quickly

converges and accurately tracks the variation of model parameters despite the large initialization error. As a result, the time-consuming and error-prone calibration is avoided. The high accuracy of model identification also verifies the robustness of proposed method against the noise corruption. In contrast, the RLS-EKF converges to values substantially away from the references, especially for R_p and C_p . This is due to the unexpected sensing of noises in both current and voltage brings non-ignorable identification bias to the identified model parameters. Moreover, the identification bias is intrinsic and will not be eliminated by involving a large amount of sample points.

According to the biased model identification, we expect that the RLS-EKF could not provide SOC estimates as accurate as the proposed FBCRLS based observer. To illustrate this, the SOC estimation results and the reference trajectory are plotted comparatively in Figure 6.11. It is observed that the proposed method projects the trajectory of reference SOC accurately and stably after a short time for erroneous initialization correction. The SOC error is constrained within 2% error bound during the entire experiment. By comparison, the RLS-EKF demonstrates a decline of accuracy as a consequence of poor noise tolerance. Although the convergence is also easy, the estimation error is obviously much larger.

To evaluate the estimation performance quantitatively, the MAE and the RMSE are used to further compare the accuracy. Moreover, the convergence time, defined as the time when the estimate starts to stabilize within the 5% error bound, is used to assess the convergence property. The aforementioned performance measures are summarized in Table 6.1 for the two applied algorithms. Evidently, the proposed method generates remarkably smaller estimation error than the RLS-EKF. This is within our expectation as the identification bias caused by noises is well compensated and model parameters are timely adapted with a higher precision. The convergence of the proposed method is slightly faster than the RLS-EKF. However, the difference in convergence speed is not significant considering the long running time. Taking all the measures into account, the comparison explicitly suggests the superiority of the proposed method over the RLS-EKF. Considering the high fidelity of both model identification and SOC estimate, the proposed FBCRLS

based SOC observer proves to be highly reliable for online applications.

Figure 6.11 SOC estimation results and SOC error for the experimental study on VRB

Table 6.1 Performance comparison of the proposed method and RLS-EKF for the experimental study on VRB

	FBCRLS based observer	RLS-EKF
MAE	0.54%	1.37%
RMSE	1.04%	3.24%
Convergence time	67 s	122 s

6.5.3 Robustness Analysis with Lithium-ion Battery

The proposed method is data driven based without details of chemical process as prerequisite. This section aims at testing the robustness of the proposed method against different battery chemistries. Experiments are thus conducted on a Samsung 18650 lithium-ion battery with the nominal capacity of 2200 mAh. The load current and terminal voltage profiles are shown in Figure 6.12. Analogous with the case of VRB, the SOC-OCV map of lithium-ion battery is also decomposed into nine linear segments here, as shown in Figure 6.13. Each segment is approximated with the linear equation shown in Eq. (6.1). The polynomial coefficients of the segments are listed in Table 6.2.

Figure 6.12 Measured load current and terminal voltage profiles for the experimental study on lithium-ion battery

Figure 6.13 SOC-OCV correlation and the piecewise treatment of the lithium-ion battery

Table 6.2 Polynomial coefficients of the SOC-OCV function of lithium-ion battery for different piecewise segments

Segment	s_1	s_2	s_3	s_4	s_5
c_0	3.2767	3.3926	3.3791	3.4407	3.4863
c_1	3.3262	0.7035	0.8461	0.5306	0.3448
Segment	s_6	s_7	s_8	s_9	
c_0	3.4196	3.1517	3.1008	3.0158	
c_1	0.4941	0.9836	1.0516	1.1518	

The results of model identification are shown in Figure 6.14. As shown, the lithium-ion battery in use is quite different to the VRB regarding the model parameters. The variation of model parameters and their dependence on SOC are more significant. However, the model parameters are still accurately adapted by the proposed FBCRLS based observer to follow their change during the entire experiment. By comparison, the RLS-EKF converges with obvious bias especially for R_p and C_p .

Figure 6.14 Identification result of model parameters for the experimental study on lithium-ion battery

Based on the online identified battery model, the SOC estimation results are plotted in Figure 6.15. Similar with the case of VRB, the estimated SOC with the proposed method tracks the reference trajectory with fast convergence, high accuracy, and good robustness to the uncertain initialization, while the accuracy of the RLS-EKF method is limited for the biased identification of model parameters. It should be mentioned that both the two algorithms generate relatively large errors between 2.8 and 3.6 h, corresponding to the SOC range between 25% and 45%. This is because

the slope of SOC-OCV correlation is very small at this region, as show in Figure 6.13 and Table 6.2, and the small slope will cause a weak observability condition for the state-space model represented by Eq. (6.14). Therefore, the relatively large errors are within expectation. The existence of such quasi-unobservable region has also been verified and discussed in ref. [42], and a dual-circuit state observer is explored to solve it. It will be interesting to integrate the proposed method with that from ref. [42] to further improve the estimation accuracy. Despite the existence of this specific region, it is explicit that the overall accuracy is quite high by using the proposed method.

Figure 6.15 SOC estimation results and SOC error for the experimental study on lithium-ion battery

The performance measures of MAE, RMSE, and convergence time are summarized in Table 6.3 for the two applied algorithms. The results reveal that the proposed method works with the lithium-ion battery accurately and stably even with large initialization errors. The improvement brought by the proposed method with regard to the existing RLS-EKF method is also significant. The proposed method is thus seen to be promising to be generalized for applications to other battery chemistries.

Table 6.3 Performance comparison of the proposed method and RLS-EKF for the experimental study on lithium-ion battery

	FBCRLS based observer	RLS-EKF
MAE	0.81%	1.65%
RMSE	1.62%	2.67%
Convergence time	167 s	268 s

6.6 Conclusions

The existing co-estimation methods are shown to yield identification bias thus lose robustness when the measurements are subject to noises. To tackle this difficulty, this chapter proposes an integrated technique for online unbiased model identification and SOC estimation by applying real-time noise statistics estimate and noise effect compensation. Simulation and experimental studies suggest that the proposed method accurately estimates the noise variances and tracks the changes of model parameters without bias. Due to the enhanced battery model identification, the SOC estimate is shown to be highly authentic whilst the convergence speed is not compromised. The proposed method also proves to outperform the RLS-EKF as a typical co-estimation method in terms of estimation accuracy and convergence speed. As a data-driven based approach, the proposed method requires only the onboard measured current and voltage signals so its application to a wide range of other battery chemistries is promising.

CHAPTER 7 Conclusions and Recommendations

7.1 Conclusions

The development of high-fidelity algorithms for the online estimation of the key battery states of VRB has been focused in this thesis, aiming at improving the reliability, efficiency, and longevity of the VRB system. The adaptive battery modeling and the online estimation of essential battery states have been investigated as the major work.

A model-based peak power estimator is proposed. The first-order RC model is applied for VRB modeling. The OCV as an important variable in the battery model is measured with an open-circuit cell. Considering the uncertainties of model parameters, they are online identified with both the RLS and EKF. A simulation study has been carried out to compare the two algorithms on some key performance measures including the convergence time, MAE, RMSE, and CPU time. Results suggest that the RLS is more appropriate for the online identification of the used model. Based on the online identified battery model, an online adaptive peak power estimator is proposed by incorporating multiple constraints on current, voltage, and battery SOC. Experimental results on a lab-scale VRB system suggest that the proposed method can accurately adapt the time varying model parameters and thus provide a high modeling accuracy. Both the peak current and the corresponding peak power have been verified to be highly authentic with a specifically designed “two-step verification” method. The selection of prediction time horizon is also found to affect the allowable peak power largely.

As an enhancement, a new model identification method is proposed without the open-circuit cell as a requirement, which contributes to simplifying the system configuration of VRB. The OCV is online estimated with the online adapted battery model and the SOC is further determined with the SOC-OCV look-up table. In this way, the estimation of model parameters and OCV are fully decoupled so that the cross interference is avoided. A comprehensive analysis on the model sensitivity,

stability, and accuracy is performed, suggesting the use of multiple timescales for different estimators. Experimental results suggest that the multi-timescale estimator is accurate in both model parameterization and SOC estimate with a high robustness against the initialization uncertainty and the operating condition variation. The robustness of the multi-timescale estimator to the battery aging is also satisfactory within an aging degree of 14.78%.

Following that, the joint estimation of SOC and instantaneous capacity is investigated for the VRB based on an online identified battery model. Unlike the existing model-based observers, a novel joint estimator is proposed which consists of two parts, i.e. a simple OCV estimator and an EKF based state estimator. A general framework of the OCV estimator that can be applied to multi-order RC models is derived. Further, the SOC and capacity are jointly estimated with a state observer which uses the online estimated OCV as system measurement. The proposed joint estimator proves to compress the filter order effectively thus has the potential to improve the computational efficiency and numerical stability. The proposed method has been compared with the RLS-EKF as one of the state-of-the-art methods and the results demonstrate that the proposed method is superior in the estimation accuracy, convergence speed, and computational cost. The proposed method is also verified to be robust against the change of operating conditions. Meanwhile, its robustness to battery aging has proved to be satisfactory within an aging degree of 13.67%.

Lastly, the effect of measurement noises on the model identification and state estimate is studied. The existence of the sensing noises proves to cause biased identification of the model parameters. A novel FBCRLS based observer is proposed to address the noise corruption and further to estimate the time varying model parameters and battery SOC in real time. The noise statistics are online estimated to allow compensating the noise effects. A simulation study has been carried out to compare the proposed method with the RLS-EKF as one of the most advanced methods. Simulation results show that the proposed method identifies the model parameters more accurately and thus achieves a higher precision on SOC estimate. Extra model uncertainties exist in real applications so that a lab-scale

experiment is conducted to evaluate the feasibility of the proposed method. Similar conclusions are drawn from the experimental study, i.e. the proposed method contributes to compensating the noise effects and improving the accuracy of both the model identification and the SOC estimate. As a data-driven based method needing only the onboard measured current and voltage, the proposed method has also been verified to be implementable on the lithium-ion battery.

7.2 Recommendations for Future Works

Notwithstanding the progress made so far in this thesis, several other topics in the field of BMS especially for thermal modeling, more accurate battery modeling, new categories of estimation methods, and some other relevant issues are worthy of pursuing for the future work.

7.2.1 Temperature Effect and Thermal Modeling

In this thesis, the temperature effect has been ignored to ease the calculation. The temperature affects both the SOC-OCV correlation and the model parameters from the theoretical perspective. However, as has been discussed in Section 5.4.2, the effect of temperature on SOC-OCV correlation is subtle enough to be ignored for the case of VRB. The model parameters, i.e. R_s , R_p , and C_p , are also affected by the working temperature. However, the proposed methods use online model adaption so the changes of model parameters can be well tracked. Therefore, even though the thermal model is not included in the proposed methods, the results are still accurate in the scope of the topics in this thesis. However, this is not true for the case of lithium-ion batteries. It is well known that lithium-ion batteries work within a very wide temperature range in real applications considering their high power density. While the proposed online model adaption can automatically track the changes of model parameters caused by temperature variation, the temperature effect on SOC-OCV correlation cannot be ignored. To this end, it is recommended to explore a three-dimensional map for OCV, i.e. expressing the OCV as a function of both SOC and temperature, to allow accurate model-based estimations. By incorporating the temperature effect, the state estimation methods throughout this thesis can be

extended to be adoptable within a broad temperature range without losing accuracy. This is especially important for the power batteries like lithium-ion batteries.

Although the temperature effect on the online state estimation is ignorable for the VRB, it has important impacts to some other system-level issues, for example the design of cooling systems. The thermal investigation can be achieved by using temperature sensors but at the cost of increasing configuration complexity, and sometimes it may be difficult to acquire the actual temperature inside the battery. In this regard, a reliable thermal model can be considered to be integrated into the established frameworks in this thesis. The thermal modeling is also important for battery system design and cooling strategies determination. Actually, we have done some work on VRB thermal modeling, as can be referred to refs. [66, 67]. The reversible entropic heat, and the irreversible heat caused by ohmic loss, ionic loss, overpotential loss, and fluid viscosity are comprehensively modeled by a set of mathematical equations. The heat dissipation process and the final temperature response are modeled with empirical formulas for the natural cooling scenario and with the Foster network for the forced cooling scenario. Such thermal models are computational easy thus are quite promising to be used to monitor the electrolyte temperature in real time. Therefore, an important topic for the future work is to incorporate these thermal models to the proposed algorithms to enhance the feasibility over a wide temperature range.

7.2.2 New Type of Battery Models

Throughout this thesis, the VRB dynamics are simulated with the first-order RC model. Alternatively, the computational intelligence based models such as ANN and SVM can be further investigated to model the highly nonlinear dynamics of VRB. Such black-box models demand no exact knowledge of the battery structure or chemistries, thus bring significant convenience to the practical applications. The operating temperature, SOC, historical load current, and historical voltage are the common model inputs in the open literatures. It should be noted that the operating flow rate is a unique variable of the flow battery that impacts the voltage response, thus it will be interesting to include the flow rate as another model input to improve

the model accuracy. The black-box models are commonly trained by the offline dataset and can work accurately for the present period. With the change of the operating conditions and battery degradation, the model trained by the original dataset may lose its accuracy gradually. In this regard, the online training of the black-box models will be an interesting topic that is worth investigating.

7.2.3 New Type of State Estimation Methods

The thesis emphasizes on improving the accuracy of the state estimation by incorporating the online model identification. The computational easy methods like the pole placement-based state observer and EKF are used to make the algorithms realistic for online applications on the low-cost microcontrollers. The utilization of other more advanced adaptive filters has not been fully addressed.

In the future work, different kinds of other state estimation methods, such as SMO, AEKF, UKF, AUKF, PF, UPF, and NPF, can be also tried to compare the advantages and shortcomings. Additionally, when integrating these estimators with the online model identification methods, the stability and computational feasibility remains uncertain and deserves further investigation. In summary, the improved algorithms with higher accuracy, adequate stability, and low computational complexity are of great importance to the field of battery modeling and state monitoring.

7.2.4 Other Issues Related to Battery Management

The state of energy (SOE) is defined as the energy left in a battery compared with its maximum value. As a key parameter in BMS, it provides the critical basis of load balancing, energy deployment, and electricity security for the complex energy systems thus can be carefully addressed for the future work. The online estimation of SOE can be achieved by the model-based observers, which is similar with the SOC determination. Alternatively, the nonlinear modeling techniques such as ANN can be also tried to infer the SOE from the onboard measurable variables.

In Chapter 6, the unbiased model identification is achieved with a novel FBCRLS based observer. The proposed method is fundamentally based on the online noise

statistics estimation and compensation. However, the noise is assumed to be white thus the proposed method cannot fulfill all the real situations. In our future work, the noise attenuation and the bias compensation under the colored noise corruption will be investigated based on the developed method.

Appendix A Derivation of OCV Estimator for Second-order RC Model

The characterization equations of the second-order RC model are:

$$\begin{aligned} V_{p1}(t) &= e^{-\frac{t_s}{R_{p1}C_{p1}}} V_{p1}(t - \Delta t_c) + (1 - e^{-\frac{t_s}{R_{p1}C_{p1}}}) R_{p1} I_L(t - \Delta t_c) \\ V_{p2}(t) &= e^{-\frac{t_s}{R_{p2}C_{p2}}} V_{p2}(t - \Delta t_c) + (1 - e^{-\frac{t_s}{R_{p2}C_{p2}}}) R_{p2} I_L(t - \Delta t_c) \end{aligned} \quad (\text{A.1})$$

$$V_t(t) = V_{oc}(t) - I_L(t) R_s - V_{p1}(t) - V_{p2}(t) \quad (\text{A.2})$$

Converting Eq. (A.1) to the frequency domain yields:

$$\begin{aligned} V_{p1}(z^{-1}) &= e^{-\frac{t_s}{R_{p1}C_{p1}}} z^{-1} V_{p1}(z^{-1}) + (1 - e^{-\frac{t_s}{R_{p1}C_{p1}}}) R_{p1} z^{-1} I_L(z^{-1}) \\ V_{p2}(z^{-1}) &= e^{-\frac{t_s}{R_{p2}C_{p2}}} z^{-1} V_{p2}(z^{-1}) + (1 - e^{-\frac{t_s}{R_{p2}C_{p2}}}) R_{p2} z^{-1} I_L(z^{-1}) \end{aligned} \quad (\text{A.3})$$

By defining $\beta_1 = \exp(-t_s / R_{p1} / C_{p1})$ and $\beta_2 = \exp(-t_s / R_{p2} / C_{p2})$, V_p can be solved in the z -domain as:

$$\begin{aligned} V_{p1}(z^{-1}) &= \frac{(1 - \beta_1) R_{p1} z^{-1}}{1 - \beta_1 z^{-1}} I_L(z^{-1}) \\ V_{p2}(z^{-1}) &= \frac{(1 - \beta_2) R_{p2} z^{-1}}{1 - \beta_2 z^{-1}} I_L(z^{-1}) \end{aligned} \quad (\text{A.4})$$

According to the relationship of Eq. (A.2), the following expression can be drawn:

$$V_{oc}(z^{-1}) = V_t(z^{-1}) + \left[\frac{(1 - \beta_1) R_{p1} z^{-1}}{1 - \beta_1 z^{-1}} + \frac{(1 - \beta_2) R_{p2} z^{-1}}{1 - \beta_2 z^{-1}} + R_s \right] I_L(z^{-1}) \quad (\text{A.5})$$

Eq. (A.5) can be alternatively written as:

$$V_{oc}(z^{-1}) = V_t(z^{-1}) + \frac{\kappa_1 + \kappa_2 z^{-1} + \kappa_3 z^{-1}}{1 + \kappa_4 z^{-1} + \kappa_5 z^{-1}} I_L(z^{-1}) \quad (\text{A.6})$$

where

$$\begin{aligned}
 \kappa_1 &= R_s \\
 \kappa_2 &= (\beta_1 + \beta_2) R_s + (1 - \beta_1) R_{p1} + (1 - \beta_2) R_{p2} \\
 \kappa_3 &= \beta_1 \beta_2 R_s - (1 - \beta_1) \beta_2 R_{p1} - (1 - \beta_2) \beta_1 R_{p2} \\
 \kappa_4 &= -\beta_1 - \beta_2 \\
 \kappa_5 &= \beta_1 \beta_2
 \end{aligned} \tag{A.7}$$

Eq. (A.6) can be reversed to the discrete-time domain as:

$$\begin{aligned}
 V_{oc}(k) &= -\kappa_4 V_{oc}(k-1) - \kappa_5 V_{oc}(k-2) + V_t(k) + \kappa_4 V_t(k-1) + \kappa_5 V_t(k-2) \\
 &\quad + \kappa_1 I_L(k) + \kappa_2 I_L(k-1) + \kappa_3 I_L(k-2)
 \end{aligned} \tag{A.8}$$

By applying transposition to Eq. (A.8), the OCV can be solved as:

$$V_{oc}(k) = \hat{V}_{oc}(k) + e_2(k) \tag{A.9}$$

where

$$\begin{aligned}
 \hat{V}_{oc}(k) &= \frac{\begin{bmatrix} V_t(k) + \kappa_4 V_t(k-1) + \kappa_5 V_t(k-2) \\ + \kappa_1 I_L(k) + \kappa_2 I_L(k-1) + \kappa_3 I_L(k-2) \end{bmatrix}}{1 + \kappa_4 + \kappa_5} \\
 e_2(k) &= \frac{\kappa_4 [V_{oc}(k) - V_{oc}(k-1)] + \kappa_5 [V_{oc}(k) - V_{oc}(k-2)]}{1 + \kappa_4 + \kappa_5}
 \end{aligned} \tag{A.10}$$

The error term represented by $e_2(k)$ becomes sufficiently small according the slowly varying OCV of VRB. The derivation procedures are totally applicable to higher-order RC models but with much more complicated equations. It should be mentioned that models with more than two RC networks are not recommendable in real applications as the high order will incorporate high computational complexity and low numerical stability.

Appendix B Derivation of Cost Function under YW Based Constraint

It is validated the below equation can be written:

$$\begin{aligned}
 E(\delta_{0,k} \bar{\varphi}_{0,k}^T \bar{\theta}_k) &= E\left(\left[-\delta_{0,k} V_{q0,k} \quad \delta_{0,k} \varphi_{0,k}^T\right] \bar{\theta}_k\right) \\
 &= E(-\delta_{0,k} V_{q0,k}) + E(\delta_{0,k} \varphi_{0,k}^T \theta_k) \\
 &= -\chi_{\delta_0 V_{p0,k}} + \Gamma_{\delta_0 \varphi_0,k} \theta_k
 \end{aligned} \tag{B.1}$$

Alternatively, the term $E(\delta_{0,k} \bar{\varphi}_{0,k}^T \bar{\theta})$ can be expressed in a different form as:

$$\begin{aligned}
 E(\delta_{0,k} \bar{\varphi}_{0,k}^T \bar{\theta}) &= E\left[(\delta_k + \tilde{\delta}_k)(\bar{\varphi}_k^T + \tilde{\varphi}_k^T) \bar{\theta}_k\right] \\
 &= E(\delta_k \bar{\varphi}_k^T \bar{\theta}_k) + E(\delta_k \tilde{\varphi}_k^T \bar{\theta}_k) + E(\tilde{\delta}_k \bar{\varphi}_k^T \bar{\theta}_k) + E(\tilde{\delta}_k \tilde{\varphi}_k^T \bar{\theta}_k)
 \end{aligned} \tag{B.2}$$

The first term on the right hand becomes 0 considering Eq. (6.18), and the remaining terms on the right-hand side is also equal to 0 according to the assumptions on noise sequence. Hence, it is proved that:

$$E(\delta_{0,k} \bar{\varphi}_{0,k}^T \bar{\theta}_k) = -\chi_{\delta_0 V_{q0,k}} + \Gamma_{\delta_0 \varphi_0,k} \theta_k = 0 \tag{B.3}$$

Therefore, the cost function under the YW based constraint can be defined as

$$Cf_k = \frac{1}{2} \left\| -\chi_{\delta_0 V_{q0,k}} + \Gamma_{\delta_0 \varphi_0,k} \hat{\theta}_k \right\|_2^2.$$

Appendix C Derivation of Recursive Update for Covariance Matrices

C.1 Equally Weighted Data

In the beginning, the situation that the data are equally weighted is considered first. The covariance matrix of two vectors (p and q) is defined as:

$$\Gamma_{pq,k} = \frac{1}{k} \sum_{i=1}^k p_i q_i^T \quad (\text{C.1})$$

The recursive version can be written as:

$$\begin{aligned} \Gamma_{pq,k} &= \frac{1}{k} \left[\sum_{i=1}^{k-1} p_i q_i^T + p_k q_k^T \right] \\ &= \frac{1}{k} \left[(k-1) \Gamma_{pq,k-1} + p_k q_k^T \right] \\ &= \left(1 - \frac{1}{k} \right) \Gamma_{pq,k-1} + \frac{1}{k} p_k q_k^T \end{aligned} \quad (\text{C.2})$$

C.2 Exponentially Weighted Data

In order to give more emphasis to the most recently obtained data and discard the old data gradually, the exponential form of data weighting should be used. This can be achieved by assigning a forgetting factor (λ) to the data vector. The weighting leads to the following recursive relation

$$\begin{aligned} \sum_{i=1}^k \lambda^{k-i} p_i q_i^T &= \sum_{i=1}^{k-1} \lambda^{k-i} p_i q_i^T + p_k q_k^T \\ &= \lambda \sum_{i=1}^{k-1} \lambda^{k-1-i} p_i q_i^T + p_k q_k^T \end{aligned} \quad (\text{C.3})$$

As different weightings are assigned to the term $p_i q_i^T$, the corresponding weighted

covariance matrix estimate can no longer use the simple scaling $1/k$ as in Eq. (C.1). Instead, a weighted arithmetic mean is used as expressed by:

$$\Gamma_{pq,k} = \frac{\sum_{i=1}^k \lambda^{k-i} p_i q_i^T}{\sum_{i=1}^k \lambda^{k-i}} \quad (\text{C.4})$$

It is obvious that Eq. (C.4) can be simplified to Eq. (C.1) if the forgetting factor is equal to 1. By defining $\gamma_k = \sum_{i=1}^k \lambda^{k-i} = (1 - \lambda^k) / (1 - \lambda)$, the recursive update of Γ_{pq} is derived by incorporating Eq. (C.3) and (C.4) as:

$$\Gamma_{pq,k} = \frac{\lambda}{\gamma_k} \gamma_{k-1} \Gamma_{pq,k-1} + \frac{1}{\gamma_k} p_k q_k^T \quad (\text{C.5})$$

Considering that $\lambda \gamma_{k-1} = \gamma_k - 1$, Eq. (C.5) can be alternatively written as:

$$\Gamma_{pq,k} = \left(1 - \frac{1}{\gamma_k}\right) \Gamma_{pq,k-1} + \frac{1}{\gamma_k} p_k q_k^T \quad (\text{C.6})$$

Clearly, the similar expressions hold for $\Gamma_{p,k}$ and $\chi_{pr,k}$.

Author's Publications

1. Z. Wei, S. Meng, K. J. Tseng, T. Lim, B. H. Soong, and M. Skyllas-Kazacos, "An adaptive model for vanadium redox flow battery and its application for online peak power estimation," *Journal of Power Sources*, vol. 344, pp. 195-207, 15/3/ 2017.
2. Z. Wei, J. Zhao, D. Ji, K. J. Tseng, "A multi-timescale estimator for battery state of charge and capacity dual estimation based on an online identified model," *Applied Energy* (2017), <http://dx.doi.org/10.1016/j.apenergy.2017.02.016>.
3. Z. Wei, K. J. Tseng, N. Wai, T. M. Lim, and M. Skyllas-Kazacos, "Adaptive estimation of state of charge and capacity with online identified battery model for vanadium redox flow battery," *Journal of Power Sources*, vol. 332, pp. 389-398, 15/11/ 2016.
4. Z. Wei, T. M. Lim, M. Skyllas-Kazacos, N. Wai, and K. J. Tseng, "Online state of charge and model parameter co-estimation based on a novel multi-timescale estimator for vanadium redox flow battery," *Applied Energy*, vol. 172, pp. 169-179, 6/15/ 2016.
5. Z. Wei, S. Meng, B. Xiong, D. Ji, and K. J. Tseng, "Enhanced online model identification and state of charge estimation for lithium-ion battery with a FBCRLS based observer," *Applied Energy*, vol. 181, pp. 332-341, 11/1/ 2016.
6. Z. Wei, J. Zhao, M. Skyllas-Kazacos, and B. Xiong, "Dynamic thermal-hydraulic modeling and stack flow pattern analysis for all-vanadium redox flow battery," *Journal of Power Sources*, vol. 260, pp. 89-99, 8/15/ 2014.
7. Z. Wei, J. Zhao, and B. Xiong, "Dynamic electro-thermal modeling of all-vanadium redox flow battery with forced cooling strategies," *Applied Energy*, vol. 135, pp. 1-10, 12/15/ 2014.
8. Z. Wei, B. Xiong, D. Ji, and K. J. Tseng, "Online State of Charge and Capacity Dual Estimation with a Multi-timescale Estimator for Lithium-ion Battery," *The*

8th International Conference on Applied Energy – ICAE2016.

9. B. Xiong, J. Zhao, Z. Wei, and M. Skyllas-Kazacos, "Extended Kalman filter method for state of charge estimation of vanadium redox flow battery using thermal-dependent electrical model," *Journal of Power Sources*, vol. 262, pp. 50-61, 9/15/ 2014.
10. T. Wang, K. Tseng, J. Zhao, and Z. Wei, "Thermal investigation of lithium-ion battery module with different cell arrangement structures and forced air-cooling strategies," *Applied Energy*, vol. 134, pp. 229-238, 1/12/ 2014.

Bibliography

- [1] T. Appenzeller, "The end of cheap oil," *National Geographic*, vol. 205, pp. 80-109, 2004.
- [2] H. Rahimi-Eichi, U. Ojha, F. Baronti, and M.-Y. Chow, "Battery management system: An overview of its application in the smart grid and electric vehicles," *IEEE Industrial Electronics Magazine*, vol. 7, pp. 4-16, 2013.
- [3] P. Denholm and G. L. Kulcinski, "Life cycle energy requirements and greenhouse gas emissions from large scale energy storage systems," *Energy Conversion and Management*, vol. 45, pp. 2153-2172, 8// 2004.
- [4] H. Chen, T. N. Cong, W. Yang, C. Tan, Y. Li, and Y. Ding, "Progress in electrical energy storage system: A critical review," *Progress in Natural Science*, vol. 19, pp. 291-312, 2009.
- [5] E. Sum, M. Rychcik, and M. Skyllas-kazacos, "Investigation of the V(V)/V(IV) system for use in the positive half-cell of a redox battery," *Journal of Power Sources*, vol. 16, pp. 85-95, 10// 1985.
- [6] M. Skyllas - Kazacos, M. Rychcik, R. G. Robins, A. G. Fane, and M. A. Green, "New All - Vanadium Redox Flow Cell," *Journal of The Electrochemical Society*, vol. 133, pp. 1057-1058, 1986.
- [7] M. Skyllas-Kazacos, G. Kazacos, G. Poon, and H. Verseema, "Recent advances with UNSW vanadium-based redox flow batteries," *International Journal of Energy Research*, vol. 34, pp. 182-189, 2010.
- [8] M. R. Mohamed, P. K. Leung, and M. H. Sulaiman, "Performance characterization of a vanadium redox flow battery at different operating parameters under a standardized test-bed system," *Applied Energy*, vol. 137, pp. 402-412, 1/1/ 2015.
- [9] J. Leadbetter and L. G. Swan, "Selection of battery technology to support grid-integrated renewable electricity," *Journal of Power Sources*, vol. 216, pp. 376-386, 2012.
- [10] G. Kear, A. A. Shah, and F. C. Walsh, "Development of the all-vanadium redox flow battery for energy storage: a review of technological, financial and policy aspects," *International Journal of Energy Research*, vol. 36, pp. 1105-1120, 2012.
- [11] M. Kazacos, M. Cheng, and M. Skyllas-Kazacos, "Vanadium redox cell electrolyte optimization studies," *Journal of Applied Electrochemistry*, vol. 20, pp. 463-467, 1990/05/01 1990.

- [12] L. Lu, X. Han, J. Li, J. Hua, and M. Ouyang, "A review on the key issues for lithium-ion battery management in electric vehicles," *Journal of power sources*, vol. 226, pp. 272-288, 2013.
- [13] A. Tang, J. Bao, and M. Skyllas-Kazacos, "Dynamic modelling of the effects of ion diffusion and side reactions on the capacity loss for vanadium redox flow battery," *Journal of Power Sources*, vol. 196, pp. 10737-10747, 12/15/2011.
- [14] A. Farmann, W. Waag, A. Marongiu, and D. U. Sauer, "Critical review of on-board capacity estimation techniques for lithium-ion batteries in electric and hybrid electric vehicles," *Journal of Power Sources*, vol. 281, pp. 114-130, 2015.
- [15] X. Qiu, T. A. Nguyen, J. D. Guggenberger, M. L. Crow, and A. C. Elmore, "A field validated model of a vanadium redox flow battery for microgrids," *IEEE Transactions on Smart Grid*, vol. 5, pp. 1592-1601, 2014.
- [16] M. Skyllas-Kazacos, M. Chakrabarti, S. Hajimolana, F. Mjalli, and M. Saleem, "Progress in flow battery research and development," *Journal of The Electrochemical Society*, vol. 158, pp. R55-R79, 2011.
- [17] C. P. De Leon, A. Frías-Ferrer, J. González-García, D. Szánto, and F. C. Walsh, "Redox flow cells for energy conversion," *Journal of Power Sources*, vol. 160, pp. 716-732, 2006.
- [18] M. Skyllas-Kazacos, M. Rychick, and R. Robins, "All-vanadium redox battery," ed: Google Patents, 1988.
- [19] M. Rychcik and M. Skyllas-Kazacos, "Characteristics of a new all-vanadium redox flow battery," *Journal of Power Sources*, vol. 22, pp. 59-67, 1988.
- [20] C. P. De Leon, A. Frias-Ferrer, J. González-García, D. Szánto, and F. C. Walsh, "Redox flow cells for energy conversion," *Journal of Power Sources*, vol. 160, pp. 716-732, 2006.
- [21] M. Skyllas-Kazacos, "Secondary batteries-flow systems, vanadium redox flow batteries," ed: Elsevier: Amsterdam, 2009, pp. 444-453.
- [22] M. Skyllas-Kazacos, C. Menictas, and T. Lim, "Redox flow batteries for medium-to large-scale energy storage," *Electricity Transmission, Distribution and Storage Systems*, p. 398, 2013.
- [23] P. Zhao, H. Zhang, H. Zhou, J. Chen, S. Gao, and B. Yi, "Characteristics and performance of 10kW class all-vanadium redox-flow battery stack," *Journal of Power Sources*, vol. 162, pp. 1416-1420, 2006.
- [24] T. Hennessy and M. Kuntz, "The multiple benefits of integrating electricity storage with wind energy," in *IEEE Power Engineering Society General Meeting, 2005*, 2005, pp. 1952-1954.

- [25] A. Shah, M. Watt-Smith, and F. Walsh, "A dynamic performance model for redox-flow batteries involving soluble species," *Electrochimica Acta*, vol. 53, pp. 8087-8100, 2008.
- [26] H. Al-Fetlawi, A. Shah, and F. Walsh, "Non-isothermal modelling of the all-vanadium redox flow battery," *Electrochimica Acta*, vol. 55, pp. 78-89, 2009.
- [27] H. Al-Fetlawi, A. Shah, and F. Walsh, "Modelling the effects of oxygen evolution in the all-vanadium redox flow battery," *Electrochimica Acta*, vol. 55, pp. 3192-3205, 2010.
- [28] A. Shah, H. Al-Fetlawi, and F. Walsh, "Dynamic modelling of hydrogen evolution effects in the all-vanadium redox flow battery," *Electrochimica Acta*, vol. 55, pp. 1125-1139, 2010.
- [29] D. You, H. Zhang, and J. Chen, "A simple model for the vanadium redox battery," *Electrochimica Acta*, vol. 54, pp. 6827-6836, 11/30/ 2009.
- [30] X. Ma, H. Zhang, and F. Xing, "A three-dimensional model for negative half cell of the vanadium redox flow battery," *Electrochimica Acta*, vol. 58, pp. 238-246, 2011.
- [31] M. Vynnycky, "Analysis of a model for the operation of a vanadium redox battery," *Energy*, vol. 36, pp. 2242-2256, 2011.
- [32] H. He, R. Xiong, H. Guo, and S. Li, "Comparison study on the battery models used for the energy management of batteries in electric vehicles," *Energy Conversion and Management*, vol. 64, pp. 113-121, 2012.
- [33] S. Abu-Sharkh and D. Doerffel, "Rapid test and non-linear model characterisation of solid-state lithium-ion batteries," *Journal of Power Sources*, vol. 130, pp. 266-274, 2004.
- [34] D. W. Dees, V. S. Battaglia, and A. Bélanger, "Electrochemical modeling of lithium polymer batteries," *Journal of power sources*, vol. 110, pp. 310-320, 2002.
- [35] M. Charkhgard and M. Farrokhi, "State-of-charge estimation for lithium-ion batteries using neural networks and EKF," *IEEE transactions on industrial electronics*, vol. 57, pp. 4178-4187, 2010.
- [36] L. Xu, J. Wang, and Q. Chen, "Kalman filtering state of charge estimation for battery management system based on a stochastic fuzzy neural network battery model," *Energy Conversion and Management*, vol. 53, pp. 33-39, 2012.
- [37] W. Junping, C. Quanshi, and C. Binggang, "Support vector machine based battery model for electric vehicles," *Energy conversion and management*, vol. 47, pp. 858-864, 2006.

- [38] J. Hu, J. Hu, H. Lin, X. Li, C. Jiang, X. Qiu, *et al.*, "State-of-charge estimation for battery management system using optimized support vector machine for regression," *Journal of Power Sources*, vol. 269, pp. 682-693, 2014.
- [39] G. L. Plett, "Extended Kalman filtering for battery management systems of LiPB-based HEV battery packs: Part 2. Modeling and identification," *Journal of power sources*, vol. 134, pp. 262-276, 2004.
- [40] H. Chan, "A new battery model for use with battery energy storage systems and electric vehicles power systems," in *Power Engineering Society Winter Meeting, 2000. IEEE*, 2000, pp. 470-475.
- [41] Y. Wang, C. Zhang, and Z. Chen, "A method for state-of-charge estimation of Li-ion batteries based on multi-model switching strategy," *Applied Energy*, vol. 137, pp. 427-434, 1/1/ 2015.
- [42] Y. Zou, X. Hu, H. Ma, and S. E. Li, "Combined State of Charge and State of Health estimation over lithium-ion battery cell cycle lifespan for electric vehicles," *Journal of Power Sources*, vol. 273, pp. 793-803, 1/1/ 2015.
- [43] F. Yang, Y. Xing, D. Wang, and K.-L. Tsui, "A comparative study of three model-based algorithms for estimating state-of-charge of lithium-ion batteries under a new combined dynamic loading profile," *Applied Energy*, vol. 164, pp. 387-399, 2/15/ 2016.
- [44] H. He, R. Xiong, and J. Peng, "Real-time estimation of battery state-of-charge with unscented Kalman filter and RTOS μ COS-II platform," *Applied Energy*, vol. 162, pp. 1410-1418, 1/15/ 2016.
- [45] Y. Wang, C. Zhang, and Z. Chen, "A method for state-of-charge estimation of LiFePO₄ batteries at dynamic currents and temperatures using particle filter," *Journal of Power Sources*, vol. 279, pp. 306-311, 4/1/ 2015.
- [46] Y. Wang, C. Zhang, and Z. Chen, "A method for joint estimation of state-of-charge and available energy of LiFePO₄ batteries," *Applied Energy*, vol. 135, pp. 81-87, 12/15/ 2014.
- [47] Y. Wang, C. Zhang, and Z. Chen, "On-line battery state-of-charge estimation based on an integrated estimator," *Applied Energy*.
- [48] Z. Caiping, W. Le Yi, L. Xue, C. Wen, G. G. Yin, and J. Jiuchun, "Robust and Adaptive Estimation of State of Charge for Lithium-Ion Batteries," *IEEE Transactions on Industrial Electronics*, vol. 62, pp. 4948-4957, 2015.
- [49] Y. Hua, M. Xu, M. Li, C. Ma, and C. Zhao, "Estimation of State of Charge for Two Types of Lithium-Ion Batteries by Nonlinear Predictive Filter for Electric Vehicles," *Energies*, vol. 8, pp. 3556-3577, 2015.
- [50] X. Tang, Y. Wang, and Z. Chen, "A method for state-of-charge estimation of

- LiFePO₄ batteries based on a dual-circuit state observer," *Journal of Power Sources*, vol. 296, pp. 23-29, 11/20/ 2015.
- [51] C. Lin, H. Mu, R. Xiong, and W. Shen, "A novel multi-model probability battery state of charge estimation approach for electric vehicles using H-infinity algorithm," *Applied Energy*, vol. 166, pp. 76-83, 3/15/ 2016.
- [52] X. Hu, S. Li, and H. Peng, "A comparative study of equivalent circuit models for Li-ion batteries," *Journal of Power Sources*, vol. 198, pp. 359-367, 1/15/ 2012.
- [53] M. Verbrugge and E. Tate, "Adaptive state of charge algorithm for nickel metal hydride batteries including hysteresis phenomena," *Journal of Power Sources*, vol. 126, pp. 236-249, 2004.
- [54] M. Verbrugge and B. Koch, "Generalized recursive algorithm for adaptive multiparameter regression application to lead acid, nickel metal hydride, and lithium-ion batteries," *Journal of The Electrochemical Society*, vol. 153, pp. A187-A201, 2006.
- [55] M. Verbrugge, "Adaptive, multi-parameter battery state estimator with optimized time-weighting factors," *Journal of applied electrochemistry*, vol. 37, pp. 605-616, 2007.
- [56] R. Xiong, X. Gong, C. C. Mi, and F. Sun, "A robust state-of-charge estimator for multiple types of lithium-ion batteries using adaptive extended Kalman filter," *Journal of Power Sources*, vol. 243, pp. 805-816, 2013.
- [57] H. He, X. Zhang, R. Xiong, Y. Xu, and H. Guo, "Online model-based estimation of state-of-charge and open-circuit voltage of lithium-ion batteries in electric vehicles," *Energy*, vol. 39, pp. 310-318, 2012.
- [58] H. He, R. Xiong, X. Zhang, F. Sun, and J. Fan, "State-of-charge estimation of the lithium-ion battery using an adaptive extended Kalman filter based on an improved Thevenin model," *IEEE Transactions on Vehicular Technology*, vol. 60, pp. 1461-1469, 2011.
- [59] M. R. Mohamed, H. Ahmad, M. N. A. Seman, S. Razali, and M. S. Najib, "Electrical circuit model of a vanadium redox flow battery using extended Kalman filter," *Journal of Power Sources*, vol. 239, pp. 284-293, 10/1/ 2013.
- [60] J. Chahwan, C. Abbey, and G. Joos, "VRB modelling for the study of output terminal voltages, internal losses and performance," in *Electrical Power Conference, 2007. EPC 2007. IEEE Canada*, 2007, pp. 387-392.
- [61] L. Barote, C. Marinescu, and M. Georgescu, "VRB modeling for storage in stand-alone wind energy systems," in *PowerTech, 2009 IEEE Bucharest*, 2009, pp. 1-6.
- [62] L. Barote and C. Marinescu, "A new control method for VRB SOC

- estimation in stand-alone wind energy systems," in *Clean Electrical Power, 2009 International Conference on*, 2009, pp. 253-257.
- [63] W. Wang, B. Ge, D. Bi, and D. Sun, "Grid-connected wind farm power control using VRB-based energy storage system," in *2010 IEEE Energy Conversion Congress and Exposition*, 2010, pp. 3772-3777.
 - [64] X. Qiu, M. Crow, and A. Elmore, "A balance-of-plant vanadium redox battery system model," *IEEE Transactions on Sustainable Energy*, vol. 6, pp. 557-564, 2015.
 - [65] L. J. Ontiveros and P. E. Mercado, "Modeling of a Vanadium Redox Flow Battery for power system dynamic studies," *International Journal of Hydrogen Energy*, vol. 39, pp. 8720-8727, 5/27/ 2014.
 - [66] Z. Wei, J. Zhao, M. Skyllas-Kazacos, and B. Xiong, "Dynamic thermal-hydraulic modeling and stack flow pattern analysis for all-vanadium redox flow battery," *Journal of Power Sources*, vol. 260, pp. 89-99, 8/15/ 2014.
 - [67] Z. Wei, J. Zhao, and B. Xiong, "Dynamic electro-thermal modeling of all-vanadium redox flow battery with forced cooling strategies," *Applied Energy*, vol. 135, pp. 1-10, 12/15/ 2014.
 - [68] B. Xiong, J. Zhao, Z. Wei, and M. Skyllas-Kazacos, "Extended Kalman filter method for state of charge estimation of vanadium redox flow battery using thermal-dependent electrical model," *Journal of Power Sources*, vol. 262, pp. 50-61, 9/15/ 2014.
 - [69] Y. Zhang, J. Zhao, P. Wang, M. Skyllas-Kazacos, B. Xiong, and R. Badrinarayanan, "A comprehensive equivalent circuit model of all-vanadium redox flow battery for power system analysis," *Journal of Power Sources*, vol. 290, pp. 14-24, 9/20/ 2015.
 - [70] A. Cuadras and O. Kanoun, "SOC Li-ion battery monitoring with impedance spectroscopy," in *Systems, Signals and Devices, 2009. SSD'09. 6th International Multi-Conference on*, 2009, pp. 1-5.
 - [71] F. Huet, "A review of impedance measurements for determination of the state-of-charge or state-of-health of secondary batteries," *Journal of power sources*, vol. 70, pp. 59-69, 1998.
 - [72] S. Rodrigues, N. Munichandraiah, and A. Shukla, "A review of state-of-charge indication of batteries by means of ac impedance measurements," *Journal of power Sources*, vol. 87, pp. 12-20, 2000.
 - [73] S. Piller, M. Perrin, and A. Jossen, "Methods for state-of-charge determination and their applications," *Journal of power sources*, vol. 96, pp. 113-120, 2001.
 - [74] M. Skyllas-Kazacos and M. Kazacos, "State of charge monitoring methods

- for vanadium redox flow battery control," *Journal of Power Sources*, vol. 196, pp. 8822-8827, 10/15/ 2011.
- [75] S. Corcuera and M. Skyllas-Kazacos, "State-of-charge monitoring and electrolyte rebalancing methods for the vanadium redox flow battery," *European Chemical Bulletin*, vol. 1, pp. 511-519, 2012.
- [76] G. L. Plett, "Sigma-point Kalman filtering for battery management systems of LiPB-based HEV battery packs: Part 2: Simultaneous state and parameter estimation," *Journal of Power Sources*, vol. 161, pp. 1369-1384, 10/27/ 2006.
- [77] D. Li, J. Ouyang, H. Li, and J. Wan, "State of charge estimation for LiMn2O4 power battery based on strong tracking sigma point Kalman filter," *Journal of Power Sources*, vol. 279, pp. 439-449, 4/1/ 2015.
- [78] F. Zhang, M. M. U. Rehman, H. Wang, Y. Levron, G. Plett, R. Zane, *et al.*, "State-of-charge estimation based on microcontroller-implemented sigma-point Kalman filter in a modular cell balancing system for Lithium-Ion battery packs," in *2015 IEEE 16th Workshop on Control and Modeling for Power Electronics (COMPEL)*, 2015, pp. 1-7.
- [79] Y. Tian, B. Xia, W. Sun, Z. Xu, and W. Zheng, "A modified model based state of charge estimation of power lithium-ion batteries using unscented Kalman filter," *Journal of Power Sources*, vol. 270, pp. 619-626, 12/15/ 2014.
- [80] Z. He, M. Gao, C. Wang, L. Wang, and Y. Liu, "Adaptive state of charge estimation for Li-ion batteries based on an unscented Kalman filter with an enhanced battery model," *Energies*, vol. 6, pp. 4134-4151, 2013.
- [81] W. He, N. Williard, C. Chen, and M. Pecht, "State of charge estimation for electric vehicle batteries using unscented Kalman filtering," *Microelectronics Reliability*, vol. 53, pp. 840-847, 2013.
- [82] L. Wang, L. Wang, C. Liao, and J. Liu, "Sigma-point Kalman filter application on estimating battery SOC," in *2009 IEEE Vehicle Power and Propulsion Conference*, 2009, pp. 1592-1595.
- [83] R. Xiong, H. He, F. Sun, and K. Zhao, "Evaluation on state of charge estimation of batteries with adaptive extended Kalman filter by experiment approach," *IEEE Transactions on Vehicular Technology*, vol. 62, pp. 108-117, 2013.
- [84] F. Sun, X. Hu, Y. Zou, and S. Li, "Adaptive unscented Kalman filtering for state of charge estimation of a lithium-ion battery for electric vehicles," *Energy*, vol. 36, pp. 3531-3540, 2011.
- [85] J. Meng, G. Luo, and F. Gao, "Lithium Polymer Battery State-of-Charge Estimation Based on Adaptive Unscented Kalman Filter and Support Vector

- Machine," *IEEE Transactions on Power Electronics*, vol. 31, pp. 2226-2238, 2016.
- [86] Y. Tian, B. Xia, M. Wang, W. Sun, and Z. Xu, "Comparison study on two model-based adaptive algorithms for SOC estimation of lithium-ion batteries in electric vehicles," *Energies*, vol. 7, pp. 8446-8464, 2014.
- [87] F. Zhang, G. Liu, L. Fang, and H. Wang, "Estimation of Battery State of Charge With H-infinity Observer: Applied to a Robot for Inspecting Power Transmission Lines," *IEEE Transactions on Industrial Electronics*, vol. 59, pp. 1086-1095, 2012.
- [88] Y. He, X. Liu, C. Zhang, and Z. Chen, "A new model for State-of-Charge (SOC) estimation for high-power Li-ion batteries," *Applied Energy*, vol. 101, pp. 808-814, 2013.
- [89] L. Zhong, C. Zhang, Y. He, and Z. Chen, "A method for the estimation of the battery pack state of charge based on in-pack cells uniformity analysis," *Applied Energy*, vol. 113, pp. 558-564, 2014.
- [90] W. Waag, C. Fleischer, and D. U. Sauer, "Critical review of the methods for monitoring of lithium-ion batteries in electric and hybrid vehicles," *Journal of Power Sources*, vol. 258, pp. 321-339, 2014.
- [91] X. Chen, W. Shen, Z. Cao, and A. Kapoor, "A novel approach for state of charge estimation based on adaptive switching gain sliding mode observer in electric vehicles," *Journal of Power Sources*, vol. 246, pp. 667-678, 1/15/ 2014.
- [92] J. Xu, C. C. Mi, B. Cao, J. Deng, Z. Chen, and S. Li, "The state of charge estimation of lithium-ion batteries based on a proportional-integral observer," *IEEE Transactions on Vehicular Technology*, vol. 63, pp. 1614-1621, 2014.
- [93] Z. Chen, Y. Fu, and C. C. Mi, "State of charge estimation of lithium-ion batteries in electric drive vehicles using extended Kalman filtering," *IEEE Transactions on Vehicular Technology*, vol. 62, pp. 1020-1030, 2013.
- [94] C. Hu, B. D. Youn, and J. Chung, "A multiscale framework with extended Kalman filter for lithium-ion battery SOC and capacity estimation," *Applied Energy*, vol. 92, pp. 694-704, 2012.
- [95] R. Xiong, F. Sun, Z. Chen, and H. He, "A data-driven multi-scale extended Kalman filtering based parameter and state estimation approach of lithium-ion olymer battery in electric vehicles," *Applied Energy*, vol. 113, pp. 463-476, 1// 2014.
- [96] G. Plett, "Dual and joint EKF for simultaneous SOC and SOH estimation," in *Proceedings of the 21st Electric Vehicle Symposium (EVS21), Monaco*, 2005, pp. 1-12.

- [97] V.-H. Duong, H. A. Bastawrous, K. Lim, K. W. See, P. Zhang, and S. X. Dou, "Online state of charge and model parameters estimation of the LiFePO₄ battery in electric vehicles using multiple adaptive forgetting factors recursive least-squares," *Journal of Power Sources*, vol. 296, pp. 215-224, 2015.
- [98] Y.-H. Chiang, W.-Y. Sean, and J.-C. Ke, "Online estimation of internal resistance and open-circuit voltage of lithium-ion batteries in electric vehicles," *Journal of Power Sources*, vol. 196, pp. 3921-3932, 4/15/ 2011.
- [99] J. N. Hu, J. J. Hu, H. B. Lin, X. P. Li, C. L. Jiang, X. H. Qiu, *et al.*, "State-of-charge estimation for battery management system using optimized support vector machine for regression," *Journal of Power Sources*, vol. 269, pp. 682-693, 12/10/ 2014.
- [100] H. Sheng and J. Xiao, "Electric vehicle state of charge estimation: Nonlinear correlation and fuzzy support vector machine," *Journal of Power Sources*, vol. 281, pp. 131-137, 5/1/ 2015.
- [101] W.-Y. Chang, "Estimation of the state of charge for a LFP battery using a hybrid method that combines a RBF neural network, an OLS algorithm and AGA," *International Journal of Electrical Power & Energy Systems*, vol. 53, pp. 603-611, 2013.
- [102] Y.-S. Lee, W.-Y. Wang, and T.-Y. Kuo, "Soft computing for battery state-of-charge (BSOC) estimation in battery string systems," *IEEE Transactions on Industrial Electronics*, vol. 55, pp. 229-239, 2008.
- [103] W. Shen, K. Chau, C. Chan, and E. W. Lo, "Neural network-based residual capacity indicator for nickel-metal hydride batteries in electric vehicles," *IEEE Transactions on Vehicular Technology*, vol. 54, pp. 1705-1712, 2005.
- [104] J. C. A. Anton, P. J. G. Nieto, C. B. Viejo, and J. A. V. Vilán, "Support vector machines used to estimate the battery state of charge," *IEEE Transactions on Power Electronics*, vol. 28, pp. 5919-5926, 2013.
- [105] J. A. Anton, P. G. Nieto, F. de Cos Juez, F. S. Lasheras, M. G. Vega, and M. R. Gutierrez, "Battery state-of-charge estimator using the SVM technique," *Applied Mathematical Modelling*, vol. 37, pp. 6244-6253, 2013.
- [106] T. Hansen and C.-J. Wang, "Support vector based battery state of charge estimator," *Journal of Power Sources*, vol. 141, pp. 351-358, 2005.
- [107] Q.-S. Shi, C.-H. Zhang, and N.-X. Cui, "Estimation of battery state-of-charge using v-support vector regression algorithm," *International Journal of Automotive Technology*, vol. 9, pp. 759-764, 2008.
- [108] Y. Shen, "Adaptive online state-of-charge determination based on neuro-controller and neural network," *Energy Conversion and Management*, vol. 51, pp. 1093-1098, 2010.

- [109] J. Du, Z. Liu, and Y. Wang, "State of charge estimation for Li-ion battery based on model from extreme learning machine," *Control Engineering Practice*, vol. 26, pp. 11-19, 2014.
- [110] Q. Luo, L. Li, W. Wang, Z. Nie, X. Wei, B. Li, *et al.*, "Capacity Decay and Remediation of Nafion-based All-Vanadium Redox Flow Batteries," *ChemSusChem*, vol. 6, pp. 268-274, 2013.
- [111] C. Sun, J. Chen, H. Zhang, X. Han, and Q. Luo, "Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery," *Journal of Power Sources*, vol. 195, pp. 890-897, 2010.
- [112] E. Barsoukov, D. R. Poole, and D. L. Freeman, "Circuit and method for measurement of battery capacity fade," ed: Google Patents, 2005.
- [113] H.-T. Lin, T.-J. Liang, and S.-M. Chen, "Estimation of battery state of health using probabilistic neural network," *IEEE Transactions on Industrial Informatics*, vol. 9, pp. 679-685, 2013.
- [114] V. Pop, H. Bergveld, P. Notten, J. O. het Veld, and P. Regtien, "Accuracy analysis of the State-of-Charge and remaining run-time determination for lithium-ion batteries," *Measurement*, vol. 42, pp. 1131-1138, 2009.
- [115] M. A. Roscher, O. S. Bohlen, and D. U. Sauer, "Reliable state estimation of multicell lithium-ion battery systems," *IEEE Transactions on Energy Conversion*, vol. 26, pp. 737-743, 2011.
- [116] B. S. Bhangu, P. Bentley, D. A. Stone, and C. M. Bingham, "Nonlinear observers for predicting state-of-charge and state-of-health of lead-acid batteries for hybrid-electric vehicles," *IEEE Transactions on Vehicular Technology*, vol. 54, pp. 783-794, 2005.
- [117] B. Bhangu, P. Bentley, D. Stone, and C. Bingham, "Observer techniques for estimating the state-of-charge and state-of-health of VRLABs for hybrid electric vehicles," in *2005 IEEE Vehicle Power and Propulsion Conference*, 2005, p. 10 pp.
- [118] F. Zhang, G. Liu, and L. Fang, "Battery state estimation using unscented kalman filter," in *Robotics and Automation, 2009. ICRA'09. IEEE International Conference on*, 2009, pp. 1863-1868.
- [119] X. Tang, X. Mao, J. Lin, and B. Koch, "Li-ion battery parameter estimation for state of charge," in *Proceedings of the 2011 American control conference*, 2011, pp. 941-946.
- [120] S. Lee, J. Kim, J. Lee, and B. Cho, "State-of-charge and capacity estimation of lithium-ion battery using a new open-circuit voltage versus state-of-charge," *Journal of power sources*, vol. 185, pp. 1367-1373, 2008.

- [121] Y. Hua, A. Cordoba-Arenas, N. Warner, and G. Rizzoni, "A multi time-scale state-of-charge and state-of-health estimation framework using nonlinear predictive filter for lithium-ion battery pack with passive balance control," *Journal of Power Sources*, vol. 280, pp. 293-312, 4/15/ 2015.
- [122] I.-S. Kim, "A technique for estimating the state of health of lithium batteries through a dual-sliding-mode observer," *IEEE Transactions on Power Electronics*, vol. 25, pp. 1013-1022, 2010.
- [123] S. Schwunk, N. Armbruster, S. Straub, J. Kehl, and M. Vetter, "Particle filter for state of charge and state of health estimation for lithium-iron phosphate batteries," *Journal of Power Sources*, vol. 239, pp. 705-710, 2013.
- [124] P. B. T. Manual, "DOE/ID-10597," ed: Revision, 2001.
- [125] F. Zheng, J. Jiang, B. Sun, W. Zhang, and M. Pecht, "Temperature dependent power capability estimation of lithium-ion batteries for hybrid electric vehicles," *Energy*, vol. 113, pp. 64-75, 2016.
- [126] R. Xiong, H. He, F. Sun, and K. Zhao, "Online estimation of peak power capability of Li-Ion batteries in electric vehicles by a hardware-in-loop approach," *Energies*, vol. 5, pp. 1455-1469, 2012.
- [127] F. Sun, R. Xiong, H. He, W. Li, and J. E. E. Aussems, "Model-based dynamic multi-parameter method for peak power estimation of lithium-ion batteries," *Applied energy*, vol. 96, pp. 378-386, 2012.
- [128] R. Xiong, H. He, F. Sun, X. Liu, and Z. Liu, "Model-based state of charge and peak power capability joint estimation of lithium-ion battery in plug-in hybrid electric vehicles," *Journal of power sources*, vol. 229, pp. 159-169, 2013.
- [129] R. Xiong, F. Sun, H. He, and T. D. Nguyen, "A data-driven adaptive state of charge and power capability joint estimator of lithium-ion polymer battery used in electric vehicles," *Energy*, vol. 63, pp. 295-308, 2013.
- [130] F. Sun, R. Xiong, and H. He, "Estimation of state-of-charge and state-of-power capability of lithium-ion battery considering varying health conditions," *Journal of Power Sources*, vol. 259, pp. 166-176, 2014.
- [131] L. Pei, C. Zhu, T. Wang, R. Lu, and C. Chan, "Online peak power prediction based on a parameter and state estimator for lithium-ion batteries in electric vehicles," *Energy*, vol. 66, pp. 766-778, 2014.
- [132] S. Wang, M. Verbrugge, J. S. Wang, and P. Liu, "Multi-parameter battery state estimator based on the adaptive and direct solution of the governing differential equations," *Journal of Power Sources*, vol. 196, pp. 8735-8741, 2011.
- [133] L. Wang, Y. Cheng, and J. Zou, "Battery available power prediction of

- hybrid electric vehicle based on improved Dynamic Matrix Control algorithms," *Journal of Power Sources*, vol. 261, pp. 337-347, 2014.
- [134] S. Wang, M. Verbrugge, J. S. Wang, and P. Liu, "Power prediction from a battery state estimator that incorporates diffusion resistance," *Journal of Power Sources*, vol. 214, pp. 399-406, 2012.
 - [135] W. Waag, C. Fleischer, and D. U. Sauer, "Adaptive on-line prediction of the available power of lithium-ion batteries," *Journal of Power Sources*, vol. 242, pp. 548-559, 2013.
 - [136] T. Feng, L. Yang, X. Zhao, H. Zhang, and J. Qiang, "Online identification of lithium-ion battery parameters based on an improved equivalent-circuit model and its implementation on battery state-of-power prediction," *Journal of Power Sources*, vol. 281, pp. 192-203, 2015.
 - [137] V. Yu and D. Chen, "Peak power prediction of a vanadium redox flow battery," *Journal of Power Sources*, vol. 268, pp. 261-268, 2014.
 - [138] A. Tang, J. McCann, J. Bao, and M. Skyllas-Kazacos, "Investigation of the effect of shunt current on battery efficiency and stack temperature in vanadium redox flow battery," *Journal of Power Sources*, vol. 242, pp. 349-356, 11/15/ 2013.
 - [139] A. Tang, J. Bao, and M. Skyllas-Kazacos, "Studies on pressure losses and flow rate optimization in vanadium redox flow battery," *Journal of Power Sources*, vol. 248, pp. 154-162, 2/15/ 2014.
 - [140] Z. Wei, T. M. Lim, M. Skyllas-Kazacos, N. Wai, and K. J. Tseng, "Online state of charge and model parameter co-estimation based on a novel multi-timescale estimator for vanadium redox flow battery," *Applied Energy*, vol. 172, pp. 169-179, 6/15/ 2016.
 - [141] Z. Wei, S. Meng, B. Xiong, D. Ji, and K. J. Tseng, "Enhanced online model identification and state of charge estimation for lithium-ion battery with a FBCRLS based observer," *Applied Energy*, vol. 181, pp. 332-341, 2016.
 - [142] Z. Wei, K. J. Tseng, N. Wai, T. M. Lim, and M. Skyllas-Kazacos, "Adaptive estimation of state of charge and capacity with online identified battery model for vanadium redox flow battery," *Journal of Power Sources*, vol. 332, pp. 389-398, 2016.
 - [143] K. J. Åström and B. Wittenmark, *Adaptive control*: Courier Corporation, 2013.
 - [144] G. L. Plett, "Extended Kalman filtering for battery management systems of LiPB-based HEV battery packs: Part 3. State and parameter estimation," *Journal of Power Sources*, vol. 134, pp. 277-292, 8/12/ 2004.
 - [145] J. Larminie, A. Dicks, and M. S. McDonald, *Fuel cell systems explained* vol.

- 2: J. Wiley Chichester, UK, 2003.
- [146] M. Mohamed, H. Ahmad, and M. Abu Seman, "Estimating the State-of-Charge of all-Vanadium Redox Flow Battery using a Divided, Open-circuit Potentiometric Cell," *Elektronika ir Elektrotechnika*, vol. 19, pp. 37-42, 2013.
 - [147] S. Roe, C. Menictas, and M. Skyllas-Kazacos, "A High Energy Density Vanadium Redox Flow Battery with 3 M Vanadium Electrolyte," *Journal of The Electrochemical Society*, vol. 163, pp. A5023-A5028, 2016.
 - [148] X. Wei, Z. Nie, Q. Luo, B. Li, B. Chen, K. Simmons, *et al.*, "Nanoporous Polytetrafluoroethylene/Silica Composite Separator as a High-Performance All-Vanadium Redox Flow Battery Membrane," *Advanced Energy Materials*, vol. 3, pp. 1215-1220, 2013.
 - [149] P. K. Leung, M. R. Mohamed, A. A. Shah, Q. Xu, and M. B. Conde-Duran, "A mixed acid based vanadium–cerium redox flow battery with a zero-gap serpentine architecture," *Journal of Power Sources*, vol. 274, pp. 651-658, 1/15/ 2015.
 - [150] F. Feng, R. Lu, G. Wei, and C. Zhu, "Online estimation of model parameters and state of charge of LiFePO₄ batteries using a novel open-circuit voltage at various ambient temperatures," *Energies*, vol. 8, pp. 2950-2976, 2015.
 - [151] Z. Wei, J. Zhao, M. Skyllas-Kazacos, and B. Xiong, "Dynamic thermal-hydraulic modeling and stack flow pattern analysis for all-vanadium redox flow battery," *Journal of Power Sources*, vol. 260, pp. 89-99, 8/15/ 2014.
 - [152] G. Dong, J. Wei, C. Zhang, and Z. Chen, "Online state of charge estimation and open circuit voltage hysteresis modeling of LiFePO₄ battery using invariant imbedding method," *Applied Energy*, vol. 162, pp. 163-171, 1/15/ 2016.
 - [153] H. He, R. Xiong, and H. Guo, "Online estimation of model parameters and state-of-charge of LiFePO₄ batteries in electric vehicles," *Applied Energy*, vol. 89, pp. 413-420, 1// 2012.
 - [154] Z. Wei, X. Li, L. Xu, and Y. Cheng, "Comparative study of computational intelligence approaches for NO_x reduction of coal-fired boiler," *Energy*, vol. 55, pp. 683-692, 6/15/ 2013.
 - [155] H. He, R. Xiong, and H. Guo, "Online estimation of model parameters and state-of-charge of LiFePO₄ batteries in electric vehicles," *Applied Energy*, vol. 89, pp. 413-420, 2012.
 - [156] R. Xiong, H. He, F. Sun, and K. Zhao, "Evaluation on State of Charge Estimation of Batteries With Adaptive Extended Kalman Filter by Experiment Approach," *IEEE Transactions on Vehicular Technology*, vol. 62, pp. 108-117, 2013.

- [157] W. Zhang, W. Shi, and Z. Ma, "Adaptive unscented Kalman filter based state of energy and power capability estimation approach for lithium-ion battery," *Journal of Power Sources*, vol. 289, pp. 50-62, 2015.
- [158] H. Wu, S. Yuan, X. Zhang, C. Yin, and X. Ma, "Model parameter estimation approach based on incremental analysis for lithium-ion batteries without using open circuit voltage," *Journal of Power Sources*, vol. 287, pp. 108-118, 8/1/ 2015.
- [159] J. Remmlinger, M. Buchholz, T. Soczka-Guth, and K. Dietmayer, "On-board state-of-health monitoring of lithium-ion batteries using linear parameter-varying models," *Journal of Power Sources*, vol. 239, pp. 689-695, 10/1/ 2013.
- [160] D. Andre, C. Appel, T. Soczka-Guth, and D. U. Sauer, "Advanced mathematical methods of SOC and SOH estimation for lithium-ion batteries," *Journal of Power Sources*, vol. 224, pp. 20-27, 2/15/ 2013.
- [161] M. Sitterly, L. Wang, G. G. Yin, and C. Wang, "Enhanced Identification of Battery Models for Real-Time Battery Management," *IEEE Transactions on Sustainable Energy*, vol. 2, pp. 300-308, 2011.
- [162] L. Liu, L. Wang, Z. Chen, C. Wang, F. Lin, and H. Wang, "Integrated System Identification and State-of-Charge Estimation of Battery Systems," *IEEE Transactions on Energy Conversion*, vol. 28, pp. 12-23, 2013.
- [163] S. Beghelli, R. P. Guidorzi, and U. Soverini, "The frisch scheme in dynamic system identification," *Automatica*, vol. 26, pp. 171-176, 1// 1990.
- [164] Y. Feng and D. Owen, "Conjugate gradient methods for solving the smallest eigenpair of large symmetric eigenvalue problems," *International Journal for Numerical Methods in Engineering*, vol. 39, pp. 2209-2229, 1996.
- [165] R. Xiong, F. Sun, X. Gong, and C. Gao, "A data-driven based adaptive state of charge estimator of lithium-ion polymer battery used in electric vehicles," *Applied Energy*, vol. 113, pp. 1421-1433, 1// 2014.
- [166] H. Rahimi-Eichi, F. Baronti, and C. Mo-Yuen, "Online Adaptive Parameter Identification and State-of-Charge Coestimation for Lithium-Polymer Battery Cells," *IEEE Transactions on Industrial Electronics*, vol. 61, pp. 2053-2061, 2014.