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Advanced Solid-State Lithium Battery and Its Safety

Zhaoyang ZHAO, Haitao HU, Zhengyou HE, Hongyi ZHU, Pooya DAVARI, and Frede BLAABJERG

Abstract—Solid-state lithium battery (SSLB) is considered as the most potential energy storage device in the next generation energy system due to its excellent safety performance. However, there are still intimidating safety issues for the SSLB, due to it being still in the development stage. This paper gives an overview of the safety of SSLBs. First, advanced solid-state battery techniques are introduced. Second, the safety issues of SSLBs are discussed. Then, the safety enhancement techniques are provided. Finally, future research opportunities are presented. This paper aims to provide a reference for researchers in the fields of electronic and electrical engineering who want to make some efforts in SSLB safety.

Index Terms—Failure, safety enhancement techniques, safety issues, solid-state lithium battery (SSLB).

NOMENCLATURE

SSLB	Solid-state lithium battery.
ANN	Artificial neural network.
ARC	Accelerating rate calorimeter.
ASD	Adjustable speed drive.
ASSB	All-solid-state battery.
BSEE	Battery energy storage system.
CB	Cell balancing.
CC-CV	Constant current-constant voltage.
EIS	Electrochemical impedance spectroscopy.
EKF	Extended Kalman filtering.
EL	Ensemble learning.
EVs	Electric vehicles.
FFT	Fast Fourier transform.
HEVs	Hybrid EVs.
KF	Kalman filtering.
K-NN	K-nearest neighbor regression.
LE	Liquid electrolyte.

LEBs	Liquid electrolyte batteries.
LIBs	Lithium-ion batteries.
LLZO	Lithium lanthanum zirconium niobium oxide.
LR	Linear regression.
NDP	Neutron depth profiling.
PC	Pulse current.
PE	Power electronic.
PI	Proportional integral.
QSSB	Quasi-solid-state battery.
RF	Random forest.
RLS	Recursive least square.
RMS	Root mean square.
SEM	Scanning electron microscopy.
SE	Solid electrolyte.
SOE	State of energy.
SOH	State of health.
SOP	State of power.
SOS	State of safety.
SOT	State of temperature.
SRC	Sinusoidal ripple current.
SSB	Solid-state battery.
SVM	Support vector machine.
sXAS	Soft X-ray absorption spectroscopy.
UKF	Unscented KF.

I. INTRODUCTION

NOWADAYS, lithium-ion batteries (LIBs) have been widely used in grid energy storage, electric vehicles, portable devices, etc. [1], [2]. Fig. 1(a) and Fig. 1(b) show the typical applications of LIBs in power systems [3] and electric vehicles (EVs)/hybrid EVs (HEVs) [4]. However, conventional LIB is composed of flammable liquid electrolytes and carbon anodes, its energy density and safety are relatively low. Some safety accidents caused by fires and explosions of LIBs have been widely reported [5], [6]. Typical cases are shown in Fig. 1(c) [7], [8].

Recently, many efforts have been made to improve the safety of LIBs, from the designing phase to the application phase of batteries. Some state-of-the-art techniques are systematically summarized in [9]–[15]. From the perspective of the application phase, some state-of-the-art thermal management techniques [9], [10], state estimation techniques [11], fault diagnosis techniques [12], [13], etc., have been reviewed in [9]–[13]. From the perspective of the designing phase, the critical progress in materials design has been summarized in [14], [15].

Although the above-mentioned methods can improve the safety of LIBs, their intrinsic safety has not been addressed.

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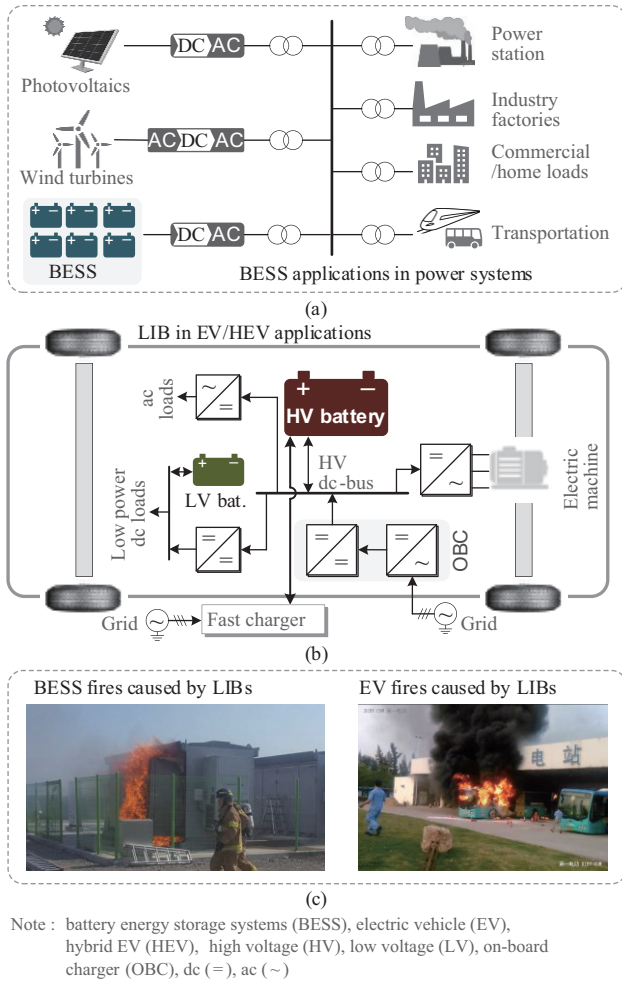


Fig. 1. Typical applications of LIBs and accidents caused by LIBs. (a) Battery energy storage system (BESS) applications in power systems [3]. (b) LIBs in electric vehicle (EV)/hybrid EV (HEV) applications [4]. (c) Typical accidents caused by LIBs [5]–[8].

Nowadays, solid-state lithium batteries (SSLBs) have caused broad attention due to the potential of achieving higher safety compared with conventional LIBs [16], [17]. However, there are still intimidating safety issues for the SSLB, due to it being still in the development stage and the design and fabrication are not entirely satisfactory. In [18], [19], the failure mechanisms of SSLBs have been summarized. Furthermore, the stability issues and safety issues of SSLBs have been thoroughly reviewed in [20], [21]. Typical failure mechanisms and safety issues are summarized in Table I.

These overviews provide summaries of SSLBs' safety issues. However, they mainly focus on the fields of materials analysis and design. In order to provide a reference for researchers in the fields of electronic and electrical engineering, this paper review the state-of-the-art solid-state lithium battery and its safety. The main contributions are given in the following.

- 1) Summarizes the state-of-the-art solid-state battery techniques and analyzes the safety of solid-state lithium batteries (SSLBs).
- 2) Discusses the safety enhancement techniques of battery, which can be used for SSLBs.

TABLE I
TYPICAL FAILURE MECHANISMS AND SAFETY ISSUES OF SSLBs [18]–[21]

Safety issue	Critical failure mechanisms
Electrochemical/chemical issue	Electrochemical reaction
	Electrode and electrolyte loss
	External mechanical stresses (e.g., nail penetration and severe impact crushing)
Mechanical issue	Internal mechanical damage (e.g., lithium dendrite, short circuit, materials volume change, internal contact problems)
	External thermal stresses (e.g., high temperature, and combustion)
Thermal issue	Internal heat generation (e.g., electrochemical reaction, overcharge, short circuit)

The rest of this paper is organized as follows: Section II reviews the advanced solid-state battery techniques. The safety issues of SSLBs are discussed in Section III. Section IV is dedicated to safety enhancement techniques. Finally, the conclusion and outlook are put forward in Section V.

II. ADVANCED SOLID-STATE BATTERY TECHNIQUES

In this section, the development of battery techniques is discussed. Then, the state-of-the-art solid-state battery (SSB) techniques are analyzed.

A. Development of Battery Techniques

According to the amount of liquid in the assembled batteries, batteries can be divided into three categories, i.e., liquid electrolyte battery, all-solid-state battery, and quasi-solid-state battery, as shown in Fig. 2.

Nowadays, the widely used LIBs are liquid electrolyte batteries (LEBs), which contain electrodes, separators, and liquid electrolytes, such as nonaqueous and aqueous electrolytes. Besides, gel electrolyte battery is also considered as liquid battery. Generally, LEBs have mature manufacturing techniques and have been widely used in various applications requiring energy storage. However, the safety issue of LEBs is considered as the main challenge. Fig. 2(a) shows the typical thermal runaway process of LEBs [22], [23].

As next-generation batteries, all-solid-state batteries (ASSBs) have been attracting wide attention. Generally, ASSBs include inorganic solid electrolyte batteries, polymer solid electrolyte batteries, composite polymer/ceramic solid electrolyte batteries, etc. However, there are still intimidating challenges in the designing and manufacturing of ASSBs. The maximum challenge of ASSBs is the interface issue, which results in the capacity, cycling, and rate performances of ASSBs being far below that of traditional LIBs. Generally, the interface issue is very complex, detail discussion can be found in [24]. Fig. 2(b) shows the typical interface issue of ASSBs [25]. Generally, the space charge layer and the interfacial layer will cause a large interfacial impedance, which reduces reaction kinetics and limits the performance of batteries. Moreover, the charging and discharging will further exacerbate the interface issue. Taking the interface between

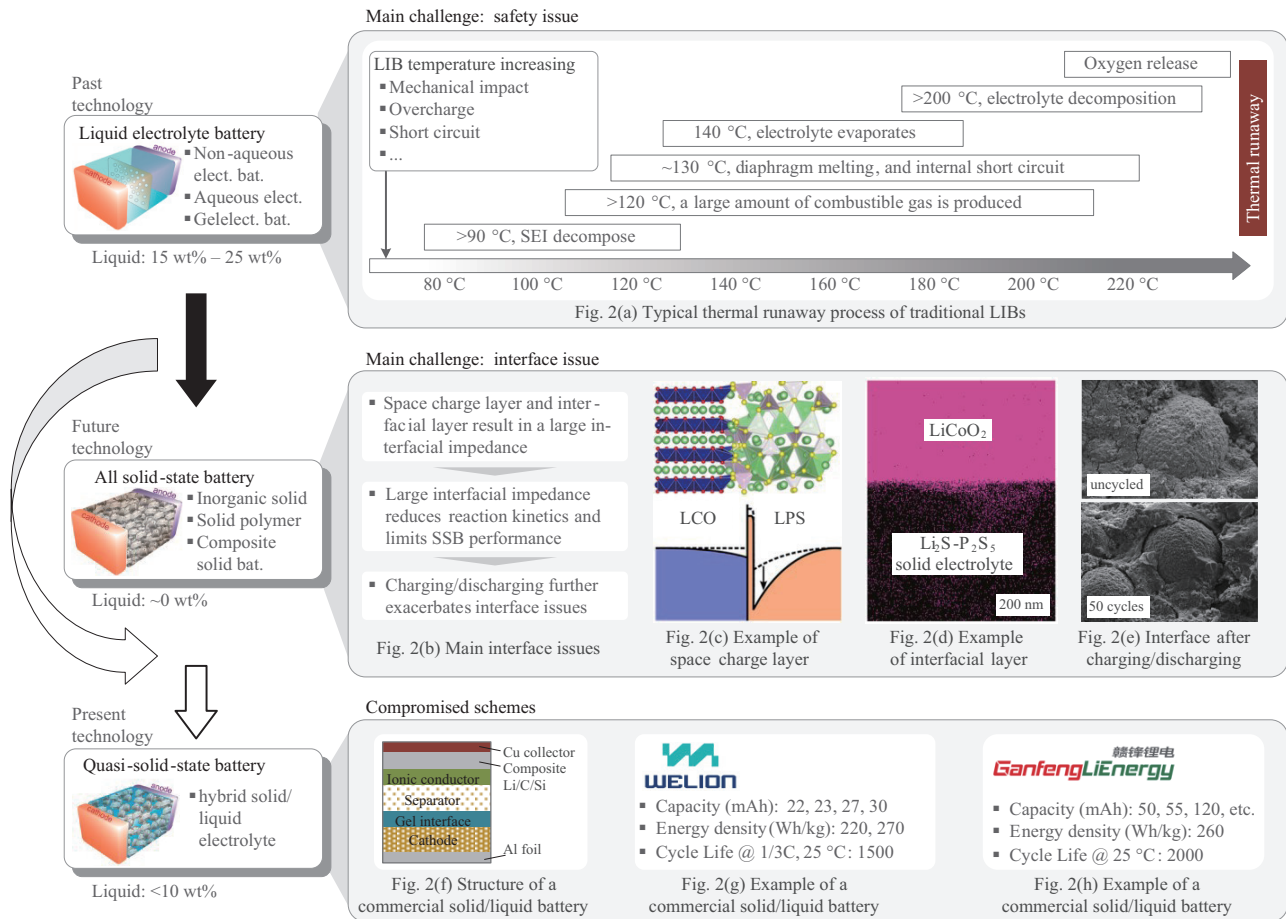


Fig. 2. Development of battery techniques [22]–[31].

LiCoO_2 cathode and $\beta\text{-Li}_3\text{PS}_4$ solid electrolyte (LCO/LPS) as an example, Fig. 2(c) shows the interface issue caused by space charge layer [26], [27]. Moreover, Fig. 2(d) shows the example of interfacial layer, where the electrodes are LiCoO_2 and $\text{Li}_2\text{S-P}_2\text{S}_5$ [28]. Furthermore, Fig. 2(e) shows the picture of SSB's interfacial layer before and after charging/discharging [29]. It can be seen that there exist obvious gaps on the interface after charging/discharging, which results in the increasing of interfacial impedance.

In order to overcome the limitations of conventional liquid electrolyte batteries and all-solid-state batteries, hybrid solid/liquid batteries have been developed. They are also known as quasi-solid-state batteries (QSSBs). Usually, a little amount of liquid phase is added on the cathode side to obtain sufficient contact between cathode particles and the solid-state electrolyte, in order to balance the performance and safety. Nowadays, the commercial “solid-state battery” all belong to quasi-solid-state batteries. Fig. 2(f) shows the structure of a commercial quasi-solid-state battery, and some commercial products are shown in Fig. 2(g) and Fig. 2(h) [30], [31].

B. State-of-the-Art SSB Techniques

Recently, the majority of studies have focused on the material development of SSBs, including the cathode, anode,

and solid electrolyte.

Generally, the available anode materials include lithium metal electrodes, graphene electrodes, silicon-based electrodes, tin-based electrodes, and metallic oxide/nitride electrodes. The composite sulfur electrodes, metallic oxide electrodes, metal sulfide electrodes, and metal fluoride electrodes can be used for the cathode of SSBs. Furthermore, polymer electrolytes, inorganic electrolytes, and composite electrolytes are widely used for solid electrolytes. Fig. 3(a) shows the classification of SSB materials. Detailed discussions of the state-of-the-art SSB materials can be found in [32]–[38].

Fig. 3(b) shows the typical assembly technologies of SSBs [20], which include heat treatment technique, cold-press technique, film technique, and roll-to-roll stack techniques. Generally, the SSB assembled using heat treatment has relatively poor interfacial and mechanical properties, and it is difficult to manufacture batteries with large capacities. The cold-press technique requires additional mechanical devices to generate presses on SSB, which has a high cost. Similarly, the film technique and roll-to-roll stack technique are also limited by battery capacity.

In summary, the materials and assembly technologies of SSBs are not mature at present. Quasi-solid batteries are feasible solutions in years to come. However, the safety of QSSBs should be considered due to the existence of liquid

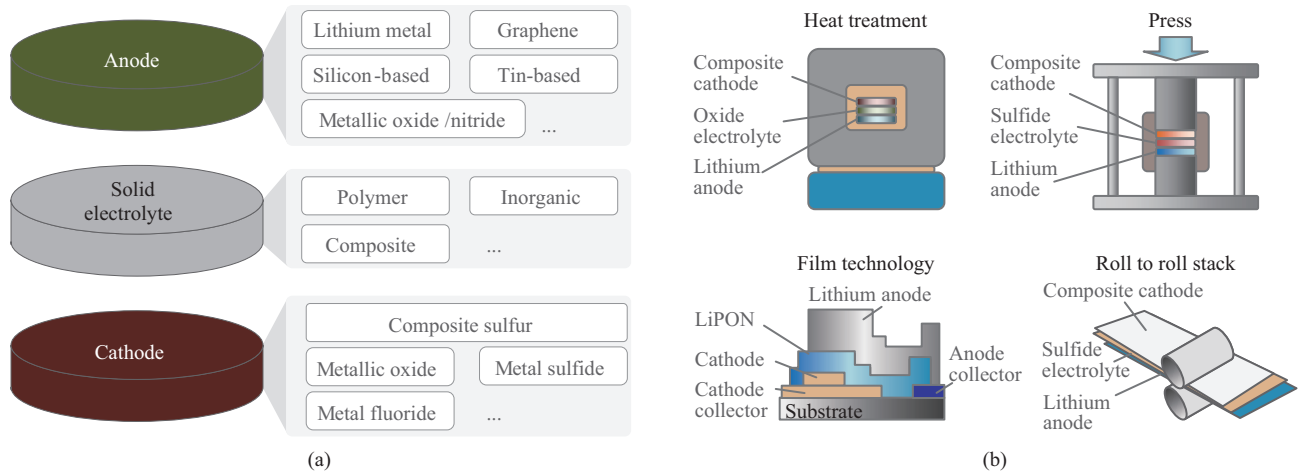


Fig. 3. State-of-the-art SSB techniques. (a) Advanced SSB materials [32]–[38]. (b) Typical assembly technologies of SSBs [20].

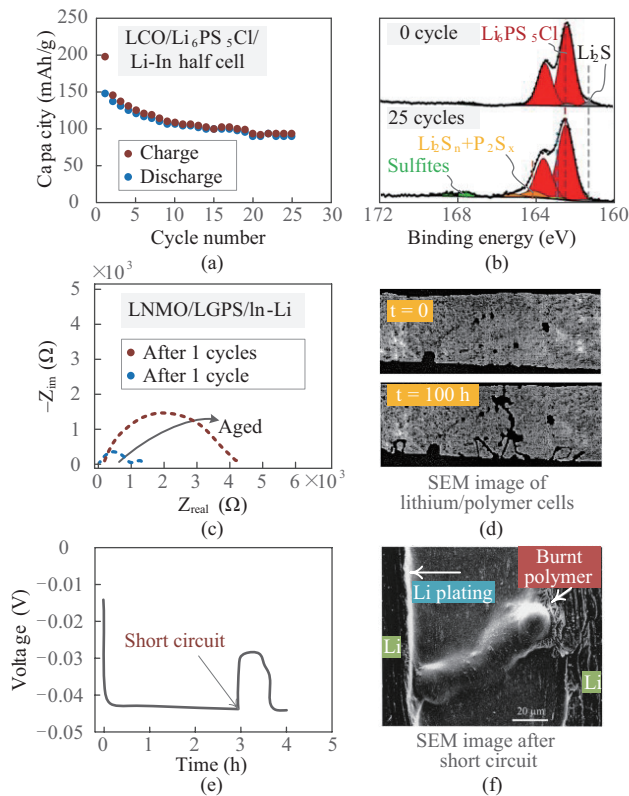


Fig. 4. Examples of failure behaviors of SSLBs. (a) Example of capacity degradation [43]. (b) X-ray photoelectron spectroscopy of the electrode surface before and after battery aging [43]. (c) Example of impedance variation [47]. (d) Example of dendritic growth [49]. (e) Example of voltage profile before and after short circuit [50]. (f) Example of short circuit [50].

electrolytes in batteries.

III. SAFETY ISSUES OF SOLID-STATE LITHIUM BATTERIES

Similar to conventional LIBs, emerging solid-state lithium batteries (SSLBs) also exist some failure behaviors caused by electric, chemical, electrochemical, mechanical, and thermal effects. In this section, the typical safety issues of SSLBs are discussed.

A. Failure Behaviors and Failure Mechanisms

Generally, it is considered that cracks caused by mechanical stresses (e.g., nail penetration and severe impact crushing) would result in short-circuiting and thermal runaway of SSLBs [21]. However, some experimental results from battery manufacturers illustrate that an SSLB can continue operating after nail penetration tests [39], [40]. At this stage, there is no clear failure analysis for SSLBs under external mechanical stresses, which is not considered in this paper. Typical failure behaviors of SSLBs include electrical parameters drift [41]–[48], internal structure change [49]–[55], and thermal runaway [56]–[58] are discussed in this part.

1) Electrical Parameters Drift

Generally, the electrical parameters, such as capacity, and impedance, will drift with the degradation of SSLBs [41], [42]. Taking LCO/Li₆PS₅Cl/Li-In half cell as an example, Fig. 4(a) shows the relationship between capacity and cycle number. It can be seen that the capacity of SSLBs decreases with the cycle number increases [43]. Generally, the electrical parameters drift is caused by the interface reaction of batteries. Fig. 4(b) shows the X-ray photoelectron spectroscopy of the electrode surface before and after battery aging. It is found that the intensity of the S2p signal of Li₂S decreases, whereas the intensity of the signal of sulfites increases [43], which demonstrates the interfacial reaction occurred.

Taking LNMO/LGPS/In-Li symmetric cells as an example, Fig. 4(c) shows the variation of electrochemical impedance spectroscopy (EIS) with the aged of SSLBs [47]. Generally, the impedance drift depends on the reaction on the solid electrolyte/electrode interface, such as space charge layer formation, element interdiffusion, and material/electrolyte interface reaction.

2) Internal Structure Change

Although solid-state electrolyte is considered can reduce the penetration of Li dendrites across electrolytes, lithium dendrite in SSBs is still a potential safety issue [49]–[52]. Taking solid

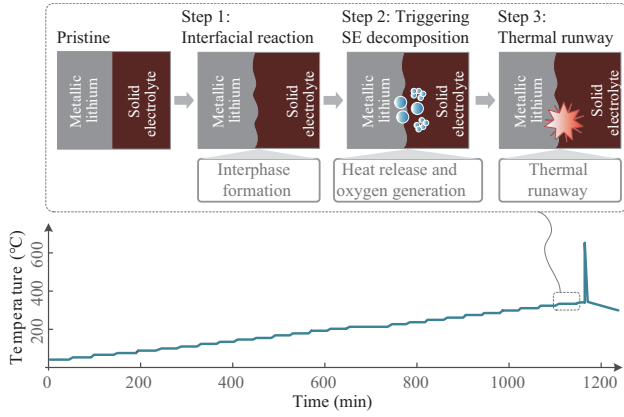


Fig. 5. Example of thermal runaway of SSLBs [57].

polymer batteries as an example, Fig. 4(d) shows its scanning electron microscopy (SEM) image, which demonstrates the growth of lithium dendrite [49]. The continuous growth of lithium dendrite may result in the internal circuit of SSBs. Taking a lithium/polymer cell as an example, Fig. 4(e) shows the voltage profile before and after an internal short occurs. Furthermore, Fig. 4(f) shows SEM image of this cell, which demonstrates the presence of a dendrite that went through the polymer.

Moreover, the volume of electrode materials will change after frequent charging and discharging. Repeated expansion and contraction will cause internal mechanically damage and contact problems, which results in the performance degradation of SSLBs [53]–[55].

3) Thermal Runaway

Similar to conventional LIBs, there exists a thermal runaway of SSBs [56]–[58]. Taking oxide solid electrolytes (SEs) with Li metal as an example, Fig. 5 shows the typical thermal runaway procedure of SSBs [57]. It can be seen that there exist three steps of this type of SE. First, the interface has formed after the contact between SEs and metallic Li. With the increase of temperature, metallic Li starts melting, and the contact of SEs and metallic Li is closer. The speed of interface reaction is accelerated. The increase of temperature and heat generated by thermal reaction further promotes the thermal decomposition of SE, which results in oxygen generation. Furthermore, the thermal runaway occurs due to the further heat generation by Li-oxygen reactions. As a result, the reactions of Li and SEs are the origin of the thermal runaway of these types of SEs. This example demonstrates that SSBs are not absolutely safe when compared with conventional LIBs.

B. Safety Performance Benchmarking With Conventional LIBs

In order to conduct the safety performance benchmarking of SSBs with conventional liquid-electrolyte LIBs, Charbonnel *et al.* [59] evaluated the safety of SSLBs with lithium lanthanum zirconium niobium oxide (LLZO) electrolytes. Fig. 6(a) and Fig. 6(b) show the characteristic curves of liquid-electrolyte LIB and LLZO-electrolyte SSB, respectively. The temperature

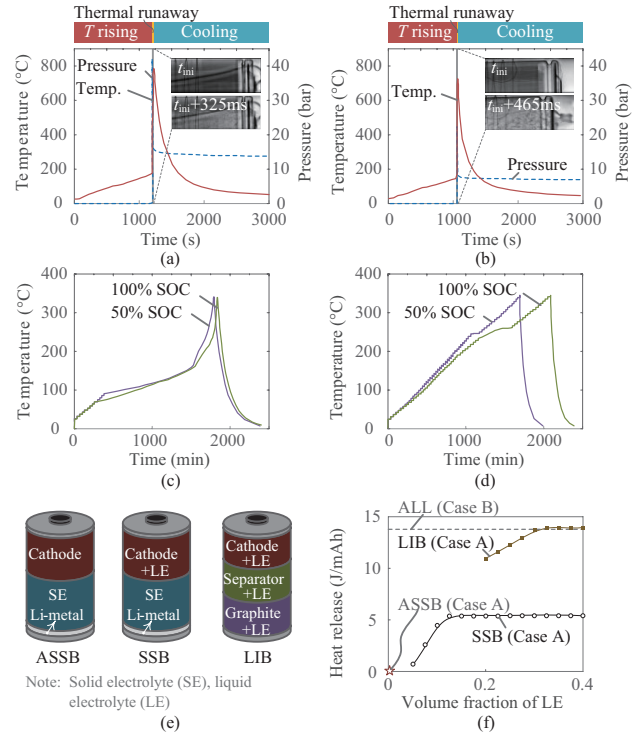


Fig. 6. Comparison of SSLBs and conventional liquid LIBs. (a) Thermal runaway procedure of a conventional LIB [59]. (b) Thermal runaway procedure of an SSB with LLZO electrolytes [59]. (c) Temperature versus time for thermal decomposition of Li/LiFePO₄ half-cells with liquid electrolytes [60]. (d) Temperature versus time for thermal decomposition of Li/LiFePO₄ half-cells with solid electrolytes [60]. (e) Typical configurations of all-solid-state batteries (ASSBs), SSBs, and LIBs [61]. (f) Heat-release results of different cells [61].

and pressure represent the surface temperature and gas pressure of battery cells during thermal runaway. There exist 3 stages in the safety test experiment. In the first stage, the batteries are heated and their temperature (T) increases. Here, the pressures have almost no change. In the second stage, a thermal runaway occurs. The temperature increases rapidly. A large amount of gas is released and the pressure increases remarkably. The upper-right portions of Fig. 6(a) and Fig. 6(b) show the X-ray images of cells, where t_{mi} indicates the initial instant of thermal runaway. It can be seen that the internal of cells have changed after the thermal runaway. In the third stage, the temperature and pressure start to decrease, which indicates the end of the thermal runaway procedure.

Based on the thermal runaway experiment, Table II summarizes the critical parameters of battery cells. Here, T_{ini} , T_{max} represent the initial temperature and maximum temperature during thermal runaway. Q , n_{gas} , and t_{TR} denote the heat release, gas quantity, and duration of thermal runaway. Referring to Fig. 6(a), Fig. 6(b) and Table II, it can be seen that T_{ini} , T_{max} , Q , n_{gas} , and t_{TR} of liquid-electrolyte LIB are slightly larger than that of SSLB.

For different types of SSLB, similar conclusions can be found. In [60], the heat release of Li/LiFePO₄ half-cell with solid polymer electrolyte and liquid electrolyte are analyzed. Fig. 6(c) and Fig. 6(d) show the experimental results of these two half cells using an accelerating rate calorimeter (ARC). It

TABLE II
TYPICAL TEST DATA OF SSB CELLS AND LIB CELLS REPORTED IN [50]

Type	$T_{ini}/^{\circ}\text{C}$	$T_{max}/^{\circ}\text{C}$	Q/kJ	$n_{\text{gas}}/\text{mmol}$	t_{TR}/ms
LIB	159	821	78.5	262	329
SSB	148	813	69.8	156	191

TABLE III
EXAMPLE OF SAFETY TEST STANDARD FOR BATTERIES [54]

Type	Test subject	Description
Cell	Over discharge	Discharge for 90 min
	Over charge	Constant-current charge to 115% SOC
	External short circuit	Connect the positive and negative terminals for 10 minutes
	Heating	Increase the temperature to $130 \pm 2^{\circ}\text{C}$ with a rate of $5^{\circ}\text{C}/\text{min}$, then hold the temperature for 30 minutes
	Temperature cycling	Set the temperature like Fig. 7(a) for 5 times
	Crush	Hold a pressure (e.g., 100 kN) for 10 minutes
Pack	Vibration	Set the random vibration parameters like Fig. 7(b) for 12 h
	Mechanical shock	Half-sine wave in $\pm z$ direction for 6 times, the accelerated speed is 7g and the pulse time is 6 ms
	Crash	Crash simulation, the accelerated speed is like Fig. 7(c)
	Crush	Similar to that for cells
	Hygrothermal cycle	Set the humidity and temperature like Fig. 7(d) and 7(e) for 5 times
	Immersion	Immerse in water for 30 minutes
	External fire	Directly exposed to flame for 70 s, then indirectly exposed for 60 s using a fire-resistant partition
	Thermal runaway	External heating or using nail penetration test
	Thermal shock	Set temperature variation between $-40 \pm 2^{\circ}\text{C}$ and $60 \pm 2^{\circ}\text{C}$ for 5 times
	Salt spray	Salt spray test for 8 h, then stewing 16 h for 6 times
	High altitude	Set atmospheric pressure as 61.2 kPa for 5 h

is found that the time to reach the maximum temperature of the solid-electrolyte cell is longer than that for liquid-electrolyte cells.

Notice that the thermal runaway results in Fig. 6(a)–(d) are caused by an external heat source, short-circuit failure also needs to be considered. In [61], thermodynamic models of all-solid-state batteries (ASSBs), SSBs, and LIBs are built to analyze their safety performance. Here, SSB refers to batteries that use a solid electrolyte with some amount of liquid electrolyte (LE), while ASSB refers to cells with no liquid electrolyte, as shown in Fig. 6(e). Considering two typical failure conditions, Fig. 6(f) shows the calculation results of heat release, where the horizontal axis represents the volume fraction of LE in batteries. Case A and Case B represent the thermal runaway resulting from an external heat source and short-circuit failure due to dendrite penetration of the electrolyte, respectively. It can be seen that the heat release of LIBs is larger than that of SSBs for Case A, and there is no heat release of ASSBs. These theoretical results are consistent with the experimental results in Fig. 6(a)–(d). For Case B, it is found that the results of these three types of cells are the same, which demonstrates the short circuit failures procedure the same heat release.

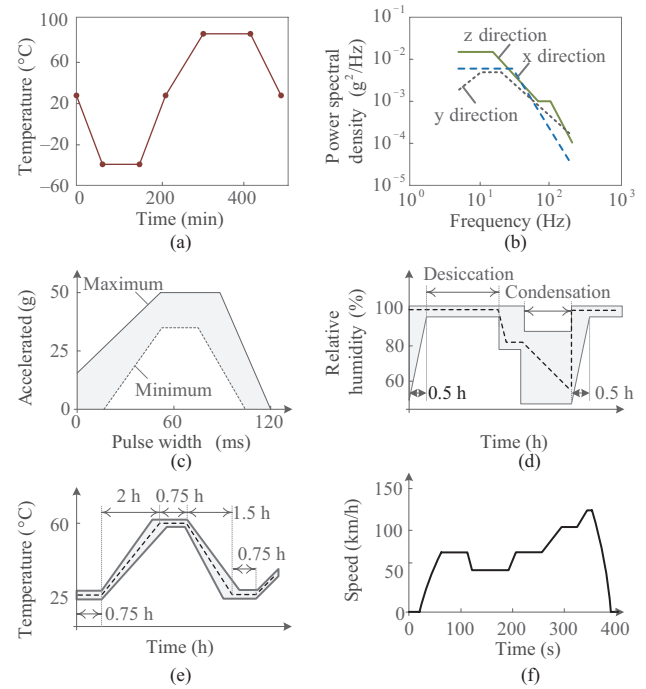


Fig. 7. Example of safety test standards and mission-profile-based methods for batteries. (a) Temperature cycling curve for cells [63]. (b) Vibration test curve [63]. (c) Schematic diagram of tolerance range of simulated collision pulse [63]. (d) Humidity cycle curve [63]. (e) Temperature cycling curve for packs [63]. (f) Example of mission profile in EVs [4].

These above-mentioned analyses demonstrate that the heat release of solid-electrolyte cells is slightly lower than that of liquid-electrolyte cells with an external heat source. However, it is not rigorous to draw a conclusion that solid-electrolyte batteries are safer than liquid-electrolyte batteries. Solid-electrolyte batteries need to be further developed.

IV. SAFETY ENHANCEMENT TECHNIQUES FOR BATTERIES

Nowadays, various safety enhancement techniques including materials modification, electrothermal management, etc., have been presented for conventional LIBs. Considering solid-state batteries are still in the development stage, the state-of-the-art safety enhancement techniques designed for LIBs are discussed in this section, in order to provide a reference for SSBs in the current stage. Notice that researchers in the fields of electronic and electrical engineering would pay more attention to electrical-related techniques including failure analysis, state estimation, cell balancing, etc., which are focused on in this section. Moreover, detailed discussions about protection, cell balancing, and lifetime improvement for LIBs are given in [62], we refer the reader to [62] for more detailed information.

A. Test Methods for Safety Evaluation

1) Safety Test Standards and Mission-Profile Based Methods

In order to evaluate the safety performance of batteries, some safety test standards have been established for commercial batteries, such as GB 38301 [63], GB 40165 [64],

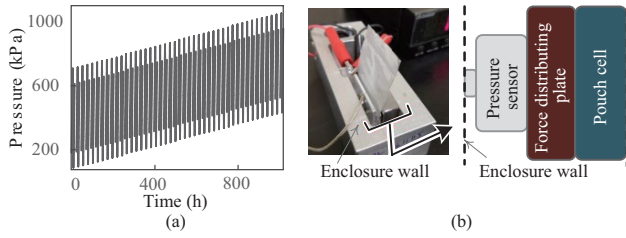


Fig. 8. Example of volume change of batteries [70]. (a) Surface pressure versus aging time for a pouch cell. (b) Experimental setup.

IEC 62133 [65], and UL 1642 [66]. Although these standards are designed for conventional LIBs, they can provide a reference for assessing SSBs at the current stage. Taking GB 38301 (standard for electric vehicles traction battery safety requirements) as an example, Table III shows the test subjects for battery cells and packs (or systems) [63], where the diagrams of temperature test, vibration test, etc., are given in Fig. 7(a)–(e).

Although the safety performance of batteries can be obtained following the above-mentioned standards, the real operating conditions cannot be reflected. Nowadays, the state-of-the-art mission-profile-based accelerated testing methods have been introduced for power electronic components and systems [67]–[69], which can be used for aging test of SSBs. A typical example of operation mission profile for EV systems is shown in Fig. 7(f) [4]. By designing a suitable power electronic circuit, the actual mission profile of SSBs can be simulated.

2) Characterization Methods

As discussed in Part A of Section III, with the degradation of SSBs, some electrical parameters and non-electrical parameters are changed. Besides the capacity, impedance, internal structure, and temperature, other parameters also can be used to characterize the state of batteries, such as volume. Taking a pouch cell as an example, Fig. 8(a) shows the relationship between surface pressure and aging time [70]. Here, the pressure is measured using a pressure sensor, which can reflect the volume change of batteries, as shown in Fig. 8(b). The experimental results demonstrate that the volume is also an indicator of batteries.

On the other hand, Fig. 4(d) and 4(f) show examples of scanning electron microscopy (SEM) images, which are widely used for the characterization of SSBs [71], [72]. Besides SEM, some *in situ* characterization methods are also can be used, such as X-ray photoelectron spectroscopy (XPS) [73], soft X-ray absorption spectroscopy (sXAS) [74], and neutron depth profiling (NDP) [75] measurement. Generally, the failure mechanism of SSBs can be investigated by using these state-of-the-art characterization methods.

B. Battery Protection and Cell Balancing

1) Battery Protection

Similar to LIB systems, there may exist faults in SSLB systems (e.g., overvoltage, undercharge, short circuits,

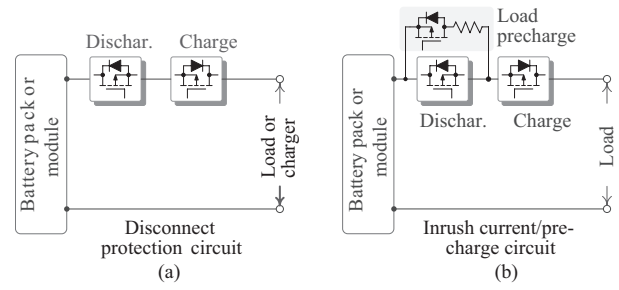


Fig. 9. Example of battery protection circuits [62], [76]. (a) Disconnect protection. (b) Inrush current/pre-charge protection.

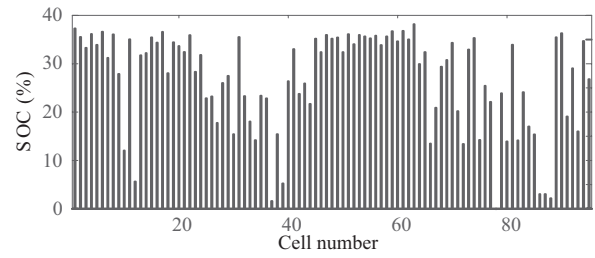


Fig. 10. Example of SOC distribution of cells in EVs after discharging [78].

overheating), which results in the demand for protection circuits. Fig. 9(a) shows a typical protection circuit for a battery system, which is also called disconnection protection [76]. Here, two MOSFETs are connected in series to form a bidirectional switch [77], and they are enabled to disconnect the circuit when a fault occurs. Generally, the charge MOSFET is used to control the flow of the charging current, and the discharge one controls the discharging current. Notice that the MOSFETs in Fig. 9(a) are placed on the high side (i.e., the positive terminal of batteries), they can also be placed on the low side (i.e., the negative terminal of batteries). Moreover, separate charge and discharge ports can also be designed for charge and discharge, respectively, which are detail discussed in [76].

Besides disconnection protection, a load inrush current protection circuit is required in a battery system, in order to limit the inrush current during the turn on phase. A typical protection circuit is shown in Fig. 9(b) [76].

2) Cell Balancing

Usually, the terminal voltage of a single battery cell is relatively low, a large number of cells are usually connected in series to meet the higher voltage demand of practical applications, such as EVs and BSEEs. However, there exist differences in cells due to manufacturing inconsistencies, and the differences will increase with the use of the batteries, which may result in overcharge and over-discharge. Taking the series-connected cells in EVs as an example, Fig. 10 shows the state of charge (SOC) distribution of cells after discharging [78]. Here, the cells have been utilized for 3 years. It can be seen that some cells are over discharge. Generally, the over-discharge and over charge caused by cell inconsistencies may result in premature degradation and safety issues of cells [79].

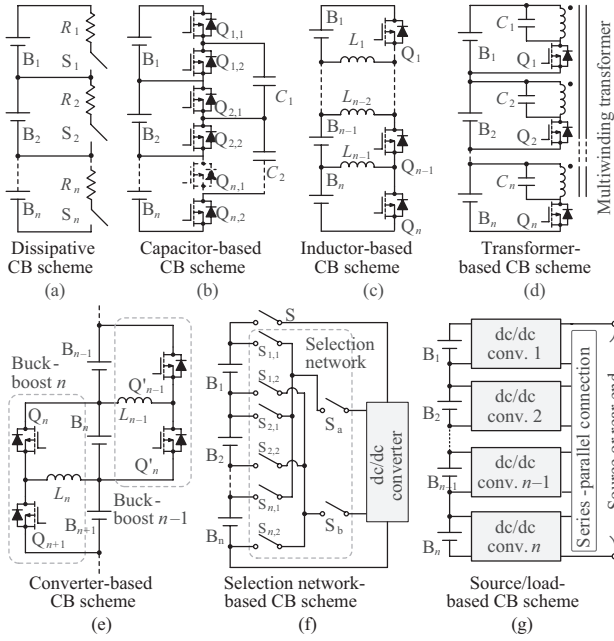


Fig. 11. Typical examples of cell balancing (CB) schemes [62]. (a) Dissipative CB scheme [62], [80]. (b) Capacitor-based CB scheme [62], [81]. (c) Inductor-based CB scheme [62], [82]. (d) Transformer-based CB scheme [62], [83]. (e) Converter-based CB scheme [62], [84]. (f) Selection network-based CB scheme [62], [85]. (g) Source/load-based CB scheme [62], [86].

Therefore, it is essential to design a cell balancing (CB) circuit to reduce the difference between cells.

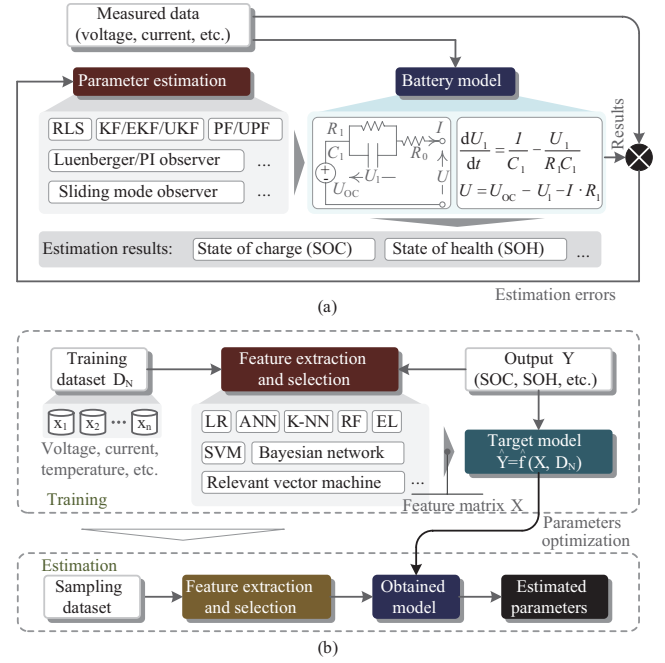
Fig. 11(a) shows a widely used CB circuit, i.e., dissipative CB scheme [80]. Although it has the advantage of low complexity, the extra energy on cells is consumed by resistance. The efficiency is relatively low, and it may cause heat problems for batteries. Considering this issue, various CB schemes including capacitor-based schemes [81], inductor-based schemes [82], transformer-based schemes [83], converter-based schemes [84], selection network-based schemes [85], and source/load-based schemes [86] have been presented. Typical examples are shown in Fig. 11. Notice that the examples in Fig. 11 are basic circuits, various improved schemes can be derived based on them. Detailed discussions can be found in [87], [88].

C. State Estimation

1) Typical State Estimation Methods

State estimation mainly refers to using voltage and current information of batteries or systems to estimate the key state of batteries, such as SOC, state of health (SOH), state of safety (SOS), state of power (SOP), state of energy (SOE), and state of temperature (SOT). Recently, various state estimation methods have been presented [89]–[92], which can be mainly divided into two categories, i.e., model-based methods and data-driven methods, as shown in Fig. 12.

Fig. 12(a) shows the typical procedure of model-based methods, which mainly includes two steps, i.e., battery modeling and parameter identifications [89], [90]. Firstly, a parameter model of batteries is built. Then, the parameters are



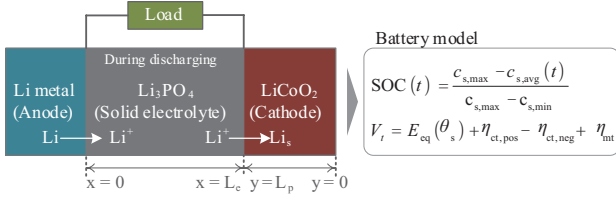
Note 1: Recursive least square (RLS), Kalman filtering (KF), extended KF(EKF), unscented KF (UKF), proportional integral (PI), linear regression (LR), artificial neural network (ANN), k-nearest neighbor regression (k-NN), randomforest (RF), ensemble learning (EL), support vector machine (SVM).

Note 2: The battery model in Fig. (a) is just for illustration. Actually, many different equivalent circuit models exist for different battery types. U_{oc} , R_0 , R_1 , C_1 , U_1 represent open-circuit voltage, ohmic resistance, polarization resistance, polarization capacitance, and polarization voltage, respectively. U and I denote terminal voltage and loop current, respectively.

Fig. 12. Typical state estimation methods for batteries. (a) Model-based method [89], [90]. (b) Data-driven method [91], [92].

estimated using parameters identification algorithms, such as recursive least square (RLS), Kalman filtering (KF), extended KF (EKF), unscented KF (UKF), proportional-integral (PI) observer, sliding mode observer, etc. [89], [90], [93]. Notice that the parameter model in Fig. 9(a) is the basic Thevenin model, which is an equivalent circuit model. Besides it, more complex second-order RC equivalent circuits, and fractional-order equivalent circuit models are also widely used for LIBs [94]. Moreover, physics-based models can effectively simulate the internal electrochemical reactions of batteries, which are also widely used in state estimation [95]. For SSLBs, physics-based models have been drawing great attention [96], [97]. Fig. 13 shows an example of a physic model of Li metal SSB [97]. Based on the method shown in Fig. 12(a), the state parameters of SSBs can be estimated.

Fig. 12(b) shows the typical procedure of data-driven methods, which mainly consist of two parts, i.e., the data training and parameters estimation. Firstly, raw data (e.g., voltage, current, temperature, etc.) and state information (e.g., SOC, SOH, aging data, etc.) of batteries are collected as training datasets [91], [92]. Then, some state-of-the-art artificial intelligence (AI) algorithms are used to obtain the target model, such as linear regression (LR), artificial neural network (ANN), k-nearest neighbor regression (k-NN), random forest (RF), ensemble learning (EL), support vector machine (SVM), etc. [91], [92]. According to the obtained estimation model, the



Note 1: The SSB is seen as a sandwich consisting of an anode (Li metal), a solid electrolyte (Li_3PO_4), and a cathode (LiCoO_2). During discharge, metallic lithium is oxidized to Li^+ ions at the negative electrode, and electrons are going to the external circuit. Li^+ ions pass through the solid electrolyte, tetravalent cobalt is reduced to trivalent cobalt at the positive electrode.

Note 2: x and y are defined in the electrolyte and cathode regions, in order to derive the governing equations. L_c and L_p represent the values of x and y , respectively. SOC, t , V_t denote the state of charge, time, and battery terminal voltage, respectively. c_s , E_{eq} , θ_s , η are the electrochemical parameters.

Fig. 13. Example of a physics-based model of SSBs [96].

parameters of models can be updated by actual data. Then, the state parameters can be obtained based on the built model and sampling datasets. Notice that the data training is performed offline, and the state estimation can be realized either offline or online.

2) Power Electronics-Based Online Monitoring

Electrochemical impedance spectroscopy (EIS) is related to the internal physical and chemical processes of batteries, which can be used to analyze the state information of batteries, such as SOC, SOH, temperature, overcharge, etc. [98]–[101]. Taking SOC and SOH as examples, Fig. 14(a) shows the relationships between EIS and SOC/SOH [98], which demonstrates that the EIS can reflect the state information of batteries.

Fig. 14(b) shows the typical test method of EIS. Usually, an excitation signal i_b (or v_b) is injected into a battery, and the corresponding response signal v_b (or i_b) is obtained. Then the impedance $z(f)$ at each frequency f is calculated using the excitation signal and response signal, i.e.,

$$z(f) = v_b(f)/i_b(f) \quad (1)$$

where, v_b and i_b represent the voltage and current of batteries. Based on (1), the EIS of a battery can be obtained. Although EIS can be measured using industrial instruments including electrochemical workstations, spectrum analyzers, impedance analyzers, etc., it cannot realize the real-time measurement during battery operation.

It is well known that power electronic (PE) circuits are widely used in battery systems to realize the functions of energy interaction, cell balancing, and battery protection. PE-based online monitoring refers to utilizing the electrical signals of PE circuits to realize online EIS measurement. Generally, the PE-based EIS monitoring can be derived into two categories, i.e., converter signal-based methods and perturbation injection-based methods.

For converter signal-based methods, the EIS is measured using the existing multifrequency signal in converter systems, such as harmonic, ripple, etc. Taking a battery-feed electric-vehicle drive system as an example, Fig. 14(c) shows the

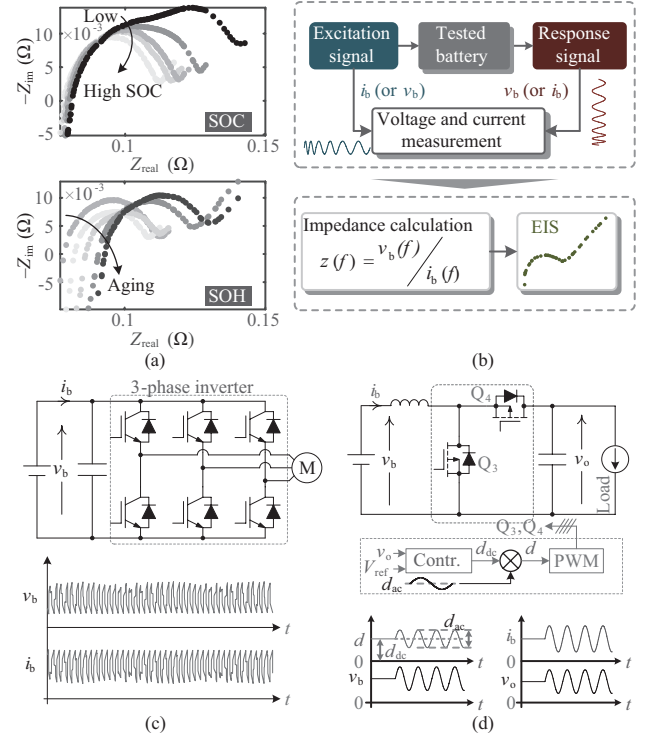


Fig. 14. Examples of EIS-based state estimation and power electronics-based EIS measurement [62]. (a) Example of EIS-based state estimation [62], [98]. (b) Typical EIS measurement method. (c) Interface converter-based EIS measurement [62], [102]. (d) Perturbation injection-based EIS measurement [62], [103].

circuit topology and typical waveforms of battery voltage v_b and battery current i_b [102]. It can be seen that v_b and i_b frequently vary due to driver or controller response, which generates abundant multifrequency information on batteries. Then, the EIS can be obtained using (1) and signal processing algorithms, such as fast Fourier transform (FFT).

For perturbation injection-based methods, perturbation signals are usually added to controllers or batteries, in order to generate multifrequency excitations. Fig. 14(d) shows an implementation example, where a buck-boost converter is used to realize the energy interaction between battery and load [103]. Here, a small perturbation signal is added to the steady-state duty cycle, which results in generating a perturbation superimposed over the battery voltage v_b and battery current i_b . Similarly, the broadband excitation signal batteries can be generated by adding a perturbation to the reference point of converters [104]. Moreover, the perturbation current can also directly add to batteries by specially designed converters [105], [106].

Besides the interface converters, cell balancing circuits also can be used for online EIS measurement [107]–[109]. Notice that converter signal-based methods are more suitable for battery-feed adjustable speed drive (ASD) systems, such as EVs, due to there exist abundant frequency information (including ripple, harmonic, and loading profile) in the system. For other applications without abundant frequency information (e.g., BESSs), perturbation injection-based methods are more suitable.

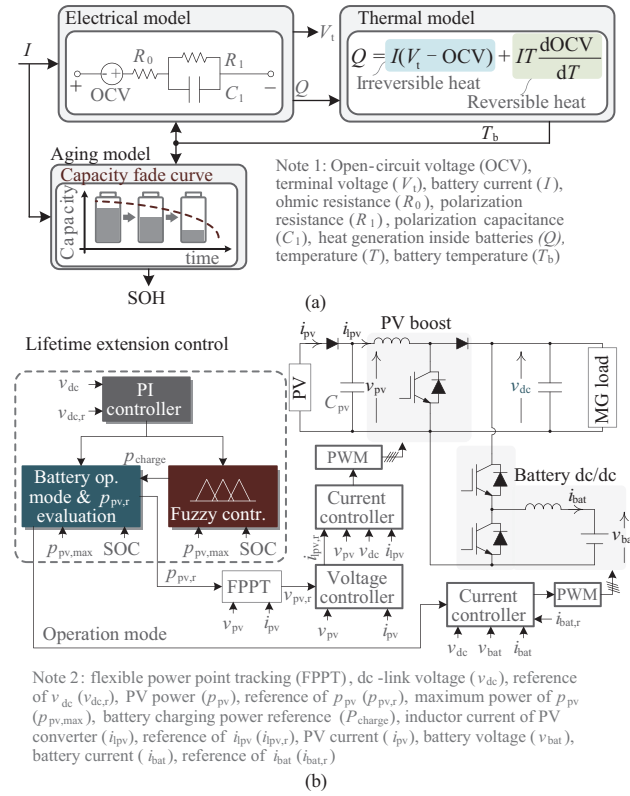


Fig. 15. Electrothermal-aging coupling model of a LIB and example of a lifetime improvement scheme. (a) Electrothermal-aging coupling model of a LIB [62], [117]. (b) Example of a lifetime improvement scheme [62], [118].

D. Lifetime Improvement

Generally, the lifetime of batteries is affected by electrical stress, such as ripples, harmonics, and charging/discharging strategies. Recent studies have demonstrated that high-frequency (greater than 10 Hz) ripples and harmonics almost have no adverse influence on LIBs' lifetime when the root mean square (RMS) values of ripples/harmonics are equal to a dc current [110], [111]. From the perspective of charging strategies, it is demonstrated that the lifetime of batteries is dependent on the RMS value of the charging current, which is not related to the charging profile [112], such as constant current-constant voltage (CC-CV) charging [113], pulse-current (PC) charging [114], and sinusoidal ripple current (SRC) charging [115].

Although it is essential to reduce the RMS value of the charging current from the perspective of safety, it may reduce other performances of batteries (e.g., charging speed). Therefore, a tradeoff between safety, speed, etc., should be considered. In [116], an electrothermal-aging coupling model of a LIB is built, as shown in Fig. 15(a). Then the optimal charging parameters are obtained using a multi-objective biogeography-based optimization algorithm, which guarantees safety and charging speed at the same time. Similar charging optimization schemes can be found in [117].

From the perspective of operation, the lifetime of batteries can be improved by specially designed control strategies.

Referring to the example shown in Fig. 15(b) [118], a fuzzy logic control algorithm is used to adjust the charging current and the PV is primarily employed, in order to reduce the stress of batteries and improve their lifetimes.

V. CONCLUSION

This paper reviews the advanced solid battery and its safety. First, the development of battery techniques and state-of-the-art solid-state batteries are discussed. Second, the main safety issues of solid-state lithium batteries (SSLBs) are summarized, including electrical parameters drift, internal structure change, and thermal runaway. Then, the safety performance of current-stage SSLBs is compared with conventional lithium-ion batteries (LIBs). Third, the existing safety enhancement techniques including safety test methods, battery protection, cell balancing, state estimation, and lifetime improvement for batteries have been discussed, which can be used for SSLBs. From the authors' point of view, future research challenges and research opportunities are summarized as follows.

A. Challenges

For solid-state batteries, the maximum challenge is that it is still in the development stage and there exist safety issues for current-stage quasi-solid-state batteries. From the perspective of battery applications instead of material design, the challenges are given in the following:

- 1) The failure behaviors and failure mechanisms of SSLBs are not very clear. There is a lack of accurate electrical models, thermal models, electrothermal models, electrochemical models, and lifetime models for current-stage SSLBs.
- 2) There is a lack of safety test standards for SSLBs.
- 3) The battery protection, cell balancing, state estimation, and lifetime improvement methods for SSLBs are referring to the existing methods for conventional LIBs. There is a lack of specially designed methods for SSLBs, which consider the characteristics of SSLBs.

B. Opportunities

The opportunities can be listed as follows:

- 1) Research safety/aging test methods and standards for SSLBs. The actual operating conditions of batteries should be considered, and mission-profile-based reliability test methods for power electronic reliability can be used as a reference [119].
- 2) Investigates electrical models, thermal models, electrothermal models, electrochemical models, lifetime models, etc., of SSLBs. Safety/realizability evaluation and improvement should be considered [119].
- 3) Designing of advanced state estimation and condition monitoring techniques for SSLBs. The state-of-the-art techniques for power electronic systems [120]–[123] and conventional LIB systems [124] can be used as references. Emerging artificial intelligence technology should be

considered [125].

- 4) Further research of protection and cell balancing circuits, on the basis of the schemes for conventional LIBs [62].
- 5) Designing of advanced charging and operating strategies on the basis of [117], [118], in order to improve the lifetimes of SSLBs.

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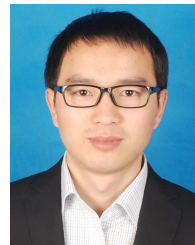
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