

# Revealing the multilevel thermal safety of lithium batteries

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## ABSTRACT

The ever-growing “endurance mileage” anxiety has been stimulating the continuous energy density raising of Li-ion batteries (LIBs) and the burgeoning of battery chemistries “beyond Li-ion”. However, if operated under abuse conditions, LIBs are easy to get thermal runaway. Encouragingly, great efforts have been devoting for achieving safer LIBs. However, the pace of thermal safety assessment has obviously lagged behind the energy density improvement of LIBs. Therefore, it is urgently needed to systematically, comprehensively and timely study the thermal safety issue of LIBs by combining different testing methods. In this review, we briefly summarize the varied testing methods for thermal safety evaluation of LIBs. Wherein, the highly-integrated accelerating rate calorimetry (ARC, an adiabatic calorimeter) technology is widely used to study the “worst case” thermal safety of LIBs at multilevel, ranging from battery materials to single cells and even battery packs. Combined with examples, the realizable specific functions of ARC in evaluating the thermal safety of LIBs are systematically summarized, and it reveals that the thermal safety of LIBs are rather complicated. Finally, critical perspectives in studying and improving thermal safety of LIBs and battery chemistries “beyond Li-ion” are provided.

## 1. Introduction

### 1.1. Background

Nowadays, rechargeable Li-ion batteries (LIBs) have been widely used in varied fields, ranging from small consumer electronics to large-scale electric vehicles (xEVs) and renewable energy storage systems (ESSs) [1–3]. The ever-growing “endurance mileage” anxiety has been stimulating the continuous energy density raising of conventional LIBs [4–7], and the burgeoning of battery chemistries “beyond Li-ion” (such as lithium metal based batteries, sodium based batteries, multivalent secondary batteries (such as magnesium, calcium, aluminum, and zinc based batteries), dual-ion batteries, capacitors, etc.) [8–11]. However, if operated under mechanical, electrical, and thermal abuse conditions, LIBs are easy to get thermal runaway (smoke, fire, and even explosion), threatening human life and property [12,13]. Every year, there are many serious accidents worldwide reported to be associated with smokes, fires and explosions of LIBs. Therefore, safety issue is a prerequisite for the practical application of LIBs. Encouragingly, at multilevel of battery material, single cell and pack, great efforts have been devoting to understand and improve the safety of LIBs [12–23]. However, the pace of thermal safety

assessment has obviously lagged behind the energy density improvement pace of LIBs, and is always biased to one point of view. Adhering to the concept of “reaching every aspect of a matter”, what we need to do is to study the LIB safety systematically, comprehensively and timely by combining different testing methods.

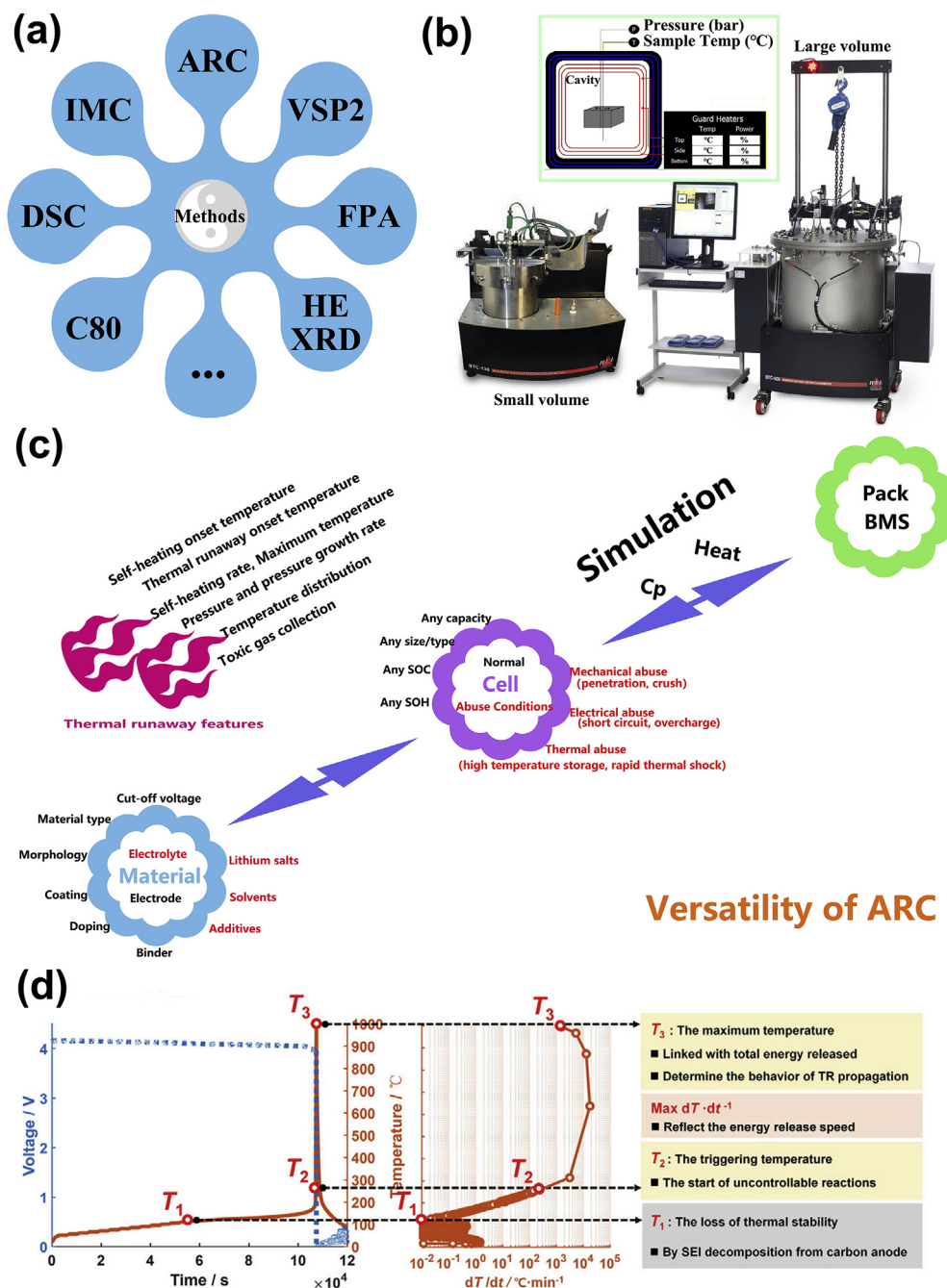
### 1.2. Methods for thermal safety evaluation

Presently, researchers have developed varied testing methods to study the thermal safety of LIBs (Fig. 1a), such as accelerating rate calorimetry (ARC) [24–27], vent sizing package 2 (VSP2) adiabatic calorimetry [28–31], isothermal microcalorimetry (IMC) [32–39], differential scanning calorimetry (DSC) [40–44], C80 micro-calorimeter [45–50], fire propagation apparatus (FPA, also called Tewarson calorimeter) [51–54], and *in-situ* high-energy X-ray diffraction technique (HEXRD) [55–57], etc. In general, IMC, DSC and C80 present high accuracy on detection of both exothermic and endothermic reactions, while ARC and VSP2 only detect exothermic reactions. Specifically, at a constant temperature, combining with an electrochemical cyler, IMC was used to study the heat generation (including reversible heat generation and irreversible heat generation) of LIBs during charge-discharge

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**Fig. 1.** (a) Varied testing methods to study the thermal safety of LIBs. (b) The illustration of BTC-130 (small volume) and BTC-500 (large volume) ARC equipment manufactured by HEL company, and the inset is a simple schematic illustration of cavity set up (HEL company). (c) The versatility of ARC technology. (d) Representative curve of ARC using typical Heat-Wait-Search (HWS) mode and corresponding thermal characteristics [15].

processes. At battery material level, DSC is usually employed to reveal the thermal stability and compatibility of electrolyte and/or electrodes. Compared to conventional DSC, a Calvet calorimeter of C80 is also used to study thermal safety at battery material level, but possesses higher accuracy, better tightness and bigger vessel volume. VSP2 is a commercially available adiabatic calorimeter, which is designed for determination of pressure related parameters at battery cell level (especially 18, 650-type LIBs). FPA belongs to a fire testing equipment and it focuses more on the combustion behavior (such as fire/heat releasing rate, toxic gas releasing rate and battery mass loss). HEXRD often is adopted as an alternative to DSC for deciphering the internal chemical reactions between the electrolyte and electrode during thermal ramping. Obviously, DSC, C80 and HEXRD are only suitable for thermal safety study at battery material level, while IMC, VSP2 and FPA only serve for thermal safety

study at battery cell level. Of course, it is difficult, costly and not necessary to let one laboratory have all aforementioned equipment. Except collaboration between laboratories, what we expect is the versatility of a single test method. Encouragingly, due to its versatile testing modes, ARC is considered as the most powerful technology to evaluate thermal safety of batteries at multilevel, ranging from battery materials to single cells and even battery packs, also ranging from normal battery charge/discharge conditions to complicated battery thermal runaway under abuse conditions.

### 1.3. Accelerating rate calorimetry (ARC) technology

As an adiabatic calorimeter, ARC (Fig. 1b) is a pivotal integrated technology to study the “worst case” thermal safety of LIBs at multilevel,

ranging from battery materials to varisized single cells and even battery packs. ARC is initially developed by Dow Chemical, then firstly commercialized by Columbia Scientific Industries, and presently manufactured mainly by three companies of HEL (Fig. 1b), THT and Netzsch. Using top, side and bottom heaters, ARC simulates an accurate adiabatic condition by keeping the cavity temperature consistent with the sample temperature, preventing the self-generated heat loss of sample (inset in Fig. 1b). The realizable specific functions of ARC (Fig. 1c) in evaluating thermal safety of LIBs are preliminarily summarized as: (I) thermal stability evaluation of electrode, electrolyte, and electrode/electrolyte, deciphering the key role of electrode engineering (material type, morphology, coating, doping, binder, etc.), electrolyte formulation (lithium salt, solvent, functional additive, etc.); (II) thermal runaway features of any (any available type, any available size, and any available capacity) LIB under any state of charge (SOC) and any state of health (SOH); (III) thermal runaway features of any LIB under abuse conditions, such as mechanical abuse (nail penetration, crush), electrical abuse (short circuit, overcharge, overdischarge) and thermal abuse (high temperature storage, rapid thermal shock, subzero temperature usage); (IV) specific heat capacity ( $C_p$ ) and heat (including reversible and irreversible heat) generation determination of any LIB under adiabatic conditions. The focused parameters or testing items of (I) (II) (III) include self-heating onset temperature, self-heating time before thermal runaway onset temperature, thermal runaway onset temperature, maximum temperature, self-heating rate (SHR,  $dT/dt$ ), pressure (also pressure growth rate (PGR,  $dP/dt$ )), temperature distribution, toxic gas collection and online visual viewing. Etc.  $C_p$  and heat determination in (IV) are needed in the thermal simulating process of single cell and battery pack, serving the rational design of battery management system (BMS).

For thermal safety testing items of (I) and (II) in ARC, typical Heat-Wait-Search (HWS) mode is usually adopted (Fig. 1d) [15]. During the heating stage, the temperature of the whole cavity will increase by 5 or 10 °C, followed by the searching mode to identify whether exothermic reactions will happen when waiting. If the heat generation rate ( $dT/dt$ ) of testing sample (battery materials or battery single cell) is smaller than the set detection limit, then next heating step starts (the stage below  $T_1$  temperature in Fig. 1d). Once the exothermic reactions cause a self-heating rate ( $dT/dt$ ) larger than the set detection limit, the heaters (top, side and bottom) of ARC will work to heat cavity according to the sample self-heating rate ( $dT/dt$ ), eliminating any heat dissipation into the surrounding and providing a quasi-adiabatic condition until the sample finally gets thermal runaway (the stage between  $T_1$  and  $T_2$  temperature in Fig. 1d). In the representative curve of ARC using typical Heat-Wait-Search (HWS) mode, three critical temperatures are chosen to clearly understand the thermal runaway behavior of LIBs:  $T_1$  denotes the self-heating onset temperature, reflecting the loss of overall thermal stability;  $T_2$  is the triggering temperature point, where the sample get severe thermal runaway accompanying with rapid temperature increase (self-heating rate ( $dT/dt$ ) will increase by several orders of magnitude);  $T_3$  represents the maximum temperature, contributing to determination of the total heat generation during thermal runaway.

In this review, we will systematically and comprehensively review the thermal safety research progress of LIBs by using the highly-integrated ARC technology. This review aims to reveal the critical role of ARC in evaluating the thermal safety of conventional LIBs and battery chemistries “beyond Li-ion”. More importantly, this review will provide meaningful perspectives to study and improve the thermal safety of batteries.

## 2. Thermal safety evaluation of Li-ion battery by ARC

### 2.1. Battery materials evaluation by ARC

#### 2.1.1. Electrolyte thermal stability

Conventional electrolytes adopt thermally unstable lithium hexafluorophosphate ( $\text{LiPF}_6$ ) as main conducting lithium salt, which is dissolved in the highly flammable carbonates (such as propylene carbonate

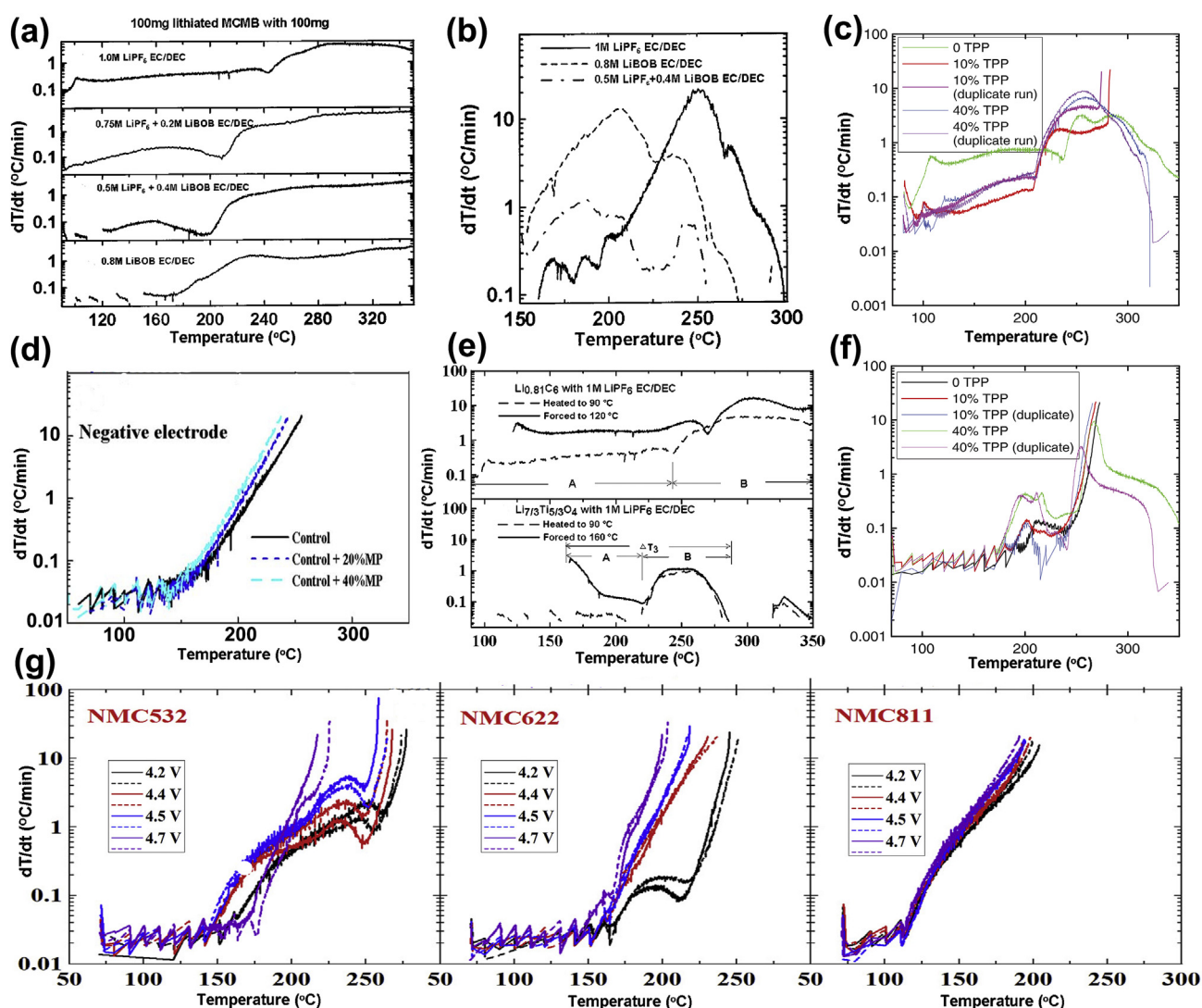
(PC), ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC), etc.) [14,20–23]. During the thermal runaway of LIBs, there are a number of chain reactions releasing heat, such as decomposition of solid electrolyte interface (SEI) layer, anode/electrolyte reactions, cathode/electrolyte reactions, self-decomposition of electrolyte, etc. [13,14]. Obviously, electrolyte plays a crucial role in determining the thermal safety of LIBs, and great efforts have been devoted to formulate high safety electrolytes [14, 20–23]. Of course, ARC technology has been adopted to evaluate the electrolyte thermal stability, which is affected by both lithium salts and organic solvents [58–67]. For example, ARC results suggested that, despite adding cyclic ether to cyclic ester based electrolyte ( $\text{LiAsF}_6$  as lithium salt) lowered the initial thermal decomposition temperature, the thermal runaway severity (SHR and PGR) was greatly reduced [58]. Moreover, replacement of  $\text{LiAsF}_6$  by  $\text{LiCF}_3\text{SO}_3$  (triflate salt) greatly raised the initial thermal decomposition temperature of electrolyte based on solvent mixture of cyclic ether and ester. ARC and DSC measurements showed that a novel lithium salt of  $\text{LiPF}_3(\text{CF}_2\text{CF}_3)_3$  (LiFAP) based electrolyte (EC-DMC-DEC) was more thermally stable than  $\text{LiPF}_6$  based electrolyte, while  $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$  (LiBETI) had the highest thermal stability [63,64]. But, the rates (SHR and PGR) of thermal reactions of LiFAP based electrolyte was greatly higher than  $\text{LiPF}_6$  based electrolyte [61,63,64]. Encouragingly, adding  $\text{LiPF}_6$  into LiFAP based electrolyte (0.5 M  $\text{LiPF}_6$  and 0.5 M LiFAP) could pronouncedly decrease SHR and PGR. Another important function of ARC is collecting generated gas byproducts, serving the electrolyte thermal decomposition or combustion mechanism study [62,67]. It was revealed by ARC and DSC that DEC solvent involved in an endothermic reaction (170 °C) before several exothermic reactions (200–325 °C), during the thermal decomposition of electrolyte (1 M  $\text{LiPF}_6$  EC/DMC/DEC) [62]. In addition, DEC solvent lowered the self-heating onset temperature, and greatly contributed to the evolution of large amounts of gas (especially flammable gases) [62, 67]. Actually, the gases (such as  $\text{H}_2$ , CO,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , HF,  $\text{POF}_3$ ,  $\text{PF}_5$ , and more other unidentified species) derived from thermal decomposition of conventional  $\text{LiPF}_6$ -carbonate electrolyte possess high risk of combustible explosion and toxic. If somebody without gas masks experiences the scene where the conventional LIBs get thermal runaway, the disgusting smell would be a nightmare. Nowadays, a large number of different types of electrolytes (with different lithium salts, solvents, and additives) have been developing for batteries [14,21]. Therefore, it is suggested that, in the future, we must give full consideration of the physical and health hazards of the gas byproducts derived from thermal decomposition of varied electrolytes.

#### 2.1.2. Anode/electrolyte thermal compatibility

High thermal stability of electrolyte does not mean or ensure the high thermal compatibility between electrode and electrolyte, and not ensure the safety enhancement of corresponding large format cells. Most of reported literatures have been devoted to study electrode/electrolyte thermal compatibility. In the thermal runaway chain reactions of LIBs, the thermal decomposition of SEI layer at anode/electrolyte interface is proved to be the first step reaction [13,14]. The anode/electrolyte thermal compatibility study mainly concentrates on revealing the effects of lithium salts [26,68–70], solvents [68,71,72], additives [73–76], binder [77,78], anode material type (including different SOC) and morphology [26,57,79–86], etc. Early in 1999, J. R. Dahn et al. proposed a convenient and instructive method for conducting reliable and reproducible ARC experiments, serving for the thermal stability study of lithiated mesocarbon microbeads (MCMB) in nonaqueous electrolyte [26]. ARC studies showed that self-heating onset temperature for lithiated MCMB in  $\text{LiBF}_4$  (EC/DEC) based electrolyte was lower than  $\text{LiPF}_6$ -based electrolyte [26]. The thermal stability of  $\text{Li}_{0.81}\text{C}_6$ /EC/DEC could be enhanced by increasing the concentration of  $\text{LiPF}_6$  or LiBOB, and it was deduced that the less reactivity of lithiated graphite anode in  $\text{LiPF}_6$ /EC/DEC than in pristine EC/DEC solvent was associated with the formation of LiF in the passivating film [26,68,70]. LiBOB based

electrolyte (1 M LiBOB or 1 M LiBOB/LiPF<sub>6</sub>) had lower reactivity with Li<sub>0.81</sub>C<sub>6</sub> than pristine LiPF<sub>6</sub>-based electrolytes (Fig. 2a) [68,69]. Unfortunately, the presence of LiBOB dramatically increased the Li<sub>0.5</sub>CoO<sub>2</sub>/electrolyte reactivity below 200 °C (Fig. 2b) [69]. Therefore, it is noted here that the adoption of thermally stable lithium salts in electrolyte not always bring the improvement of electrode/electrolyte thermal compatibility. The background scientific mechanisms are still not clearly depicted. ARC results from J. R. Dahn et al. suggested that, due to the formation of a robust passivating film, Li<sub>0.81</sub>C<sub>6</sub> showed lower reactivity in cyclic carbonate (EC) than in the linear carbonates (DMC and DEC) [68]. Various non-flammable electrolytes containing flame retardant additives/solvents have been proposed to decrease the fire risk of LIBs [14]. But, it seems like that the flame retardant ability of electrolyte is excessively emphasized, and it is always unclear that whether the flame retardant electrolyte will make the thermal stability of the battery worse nor better. The addition of triphenyl phosphate (TPP) flame retardant into control electrolyte significantly reduced the thermal reactivity (temperature dependent chemical reactivity) of

LiC<sub>6</sub>/electrolyte below 200 °C, but exhibited slightly higher self-heating rate above 200 °C (Fig. 2c) [71]. Esters (such as methyl propionate (MP), ethyl acetate (EA), etc.) are always used to enhance the electrolytes conductivity over a wide temperature range. ARC measurements indicated that the use of up to 40% MP did not enhance thermal reactivity between the charged electrodes (graphite-SiO composite anode (Fig. 2d) and Li[Ni<sub>1-x-y</sub>Co<sub>x</sub>Al<sub>y</sub>]O<sub>2</sub> cathode) and electrolyte [72]. It is pointed out that prescribing a small amount of functional additives for electrolyte will modify SEI layer, affecting not only the electrochemical performances but also the electrode/electrolyte thermal compatibility [22, 73–76,87–91]. By using ARC technology, it was revealed that, if the use of vinylene carbonate (VC) and fluoroethylene carbonate (FEC) was less than 2%, the thermal reactivity between electrolyte and lithiated graphite would be affected little [73]. Additive combination strategy is demonstrated to be more effective in enhancing the anode/electrolyte thermal compatibility [74–76]. The further addition of 1% methylene methane disulfonate (MMDS) and 1% tris(trimethylsilyl) phosphite (TTSPi) into electrolyte containing 2% VC greatly lowered self-heating



**Fig. 2.** (a) Self-heating rate (SHR) vs. temperature for samples of 100 mg of Li<sub>0.81</sub>C<sub>6</sub> and 100 mg of the indicated electrolyte as measured by ARC. (b) SHR vs. temperature for samples of 100 mg of Li<sub>0.5</sub>CoO<sub>2</sub> and 100 mg of the indicated electrolyte as measured by ARC [69]. (c) SHR vs. temperature for 70 mg lithiated graphite (LiC<sub>6</sub>), in the same mass of electrolytes containing different amounts of TPP [71]. (d) SHR vs. temperature during ARC experiments of charged graphite-SiO composite negative electrodes reacting with electrolytes containing 0%, 20% and 40% MP [72]. (e) SHR vs. temperature of 100 mg of 1 M LiPF<sub>6</sub> EC/DEC reacting with 100 mg of Li<sub>0.81</sub>C<sub>6</sub> in panel (Top) or 150 mg Li<sub>7/3</sub>Ti<sub>5/3</sub>O<sub>4</sub>, (Bottom) initially heated to 90 °C indicated with dash line or forced to a higher temperature of 120 °C (Top) or 160 °C (Bottom) in solid line [81]. (f) Self heating rate (SHR) vs. temperature of 94 mg of charged NMC (4.2 V vs. Li/Li<sup>+</sup>), in 30 mg of electrolytes containing different amounts of TPP [71]. (g) SHR vs. temperature for delithiated NMC532, NMC622 and NMC811 reacting with control electrolyte at different cut-off voltages [114].



rates between lithiated graphite and electrolyte, suggesting the formation of a more thermally stable SEI layer on the graphite anode [74]. From the perspective of formulating electrolytes, under the premise of enhancing electrochemical performances of batteries, more efforts and careful considerations are definitely needed to decipher whether the application of novel lithium salts, solvents, and additives will make the anode/electrolyte thermal compatibility worse or better.

As for engineering of carbon based anodes, factors like binder, types of carbon, SOC, specific surface area, etc. must be taken into account [26, 57,79,80]. Due to the low specific capacity, limited rate capability and poor safety characteristics of carbon materials, large amounts of novel alternatives with varied morphology (such as lithium titanate oxide ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , LTO), Si-based materials, lithium metal, conversion-type anodes, etc.) have been developed, and but their thermal reactivity with electrolytes are not given sufficient attention [3,23,81–86]. ARC showed that the self-heating onset temperature for the thermal reactions of  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  with EC/DEC solvents and with 1 M  $\text{LiPF}_6$  EC/DEC is 30 °C and about 80 °C higher, respectively, than the corresponding thermal reactions between  $\text{Li}_{0.81}\text{C}_6$  and the same electrolytes (Fig. 2e) [81]. Thus, it was concluded that LTO anode would lead to safer LIBs compared to conventional graphite anodes. Another hot anode of high capacity silicon-based (Si,  $\text{SiO}_x$ , and their carbon composites) materials have been regarded as the most promising alternatives for conventional graphite anodes [89,92–94]. Si at lithiated state had lower thermal reactivity than  $\text{Li}_{0.81}\text{C}_6$  in EC/DEC, 1 M  $\text{LiPF}_6$  EC/DEC, and 0.8 M  $\text{LiBOB}$  EC/DEC samples, even though the specific surface area of  $\text{Li}_x\text{Si}$  was larger [83,95]. Obviously, in the process of searching novel high capacity anode materials, one-sided pursuit of electrochemical performances should not be allowed, more emphasis on their thermal reactivity with electrolyte are urgently needed from the point of real applications.

### 2.1.3. Cathode/electrolyte thermal compatibility

On the other side, except the evaluation of electrolyte thermal stability and anode/electrolyte thermal compatibility, cathode/electrolyte thermal reactivity study is also very important. High electrolyte thermal stability and excellent anode/electrolyte thermal compatibility not mean the low thermal reactivity between cathode and electrolyte. The cathode/electrolyte thermal compatibility study mainly focuses on uncovering the role of lithium salts [96–102], solvents [71,72,103,104], additives [73,75,76,105], cathode material type [106–120], cathode material synthesis (method, doping, coating, etc.) [121–133], cut-off charge voltage (including SOC) [109,115,116,122–126,134,135], etc. As for lithium salts, ARC testing suggested that the thermally stable 0.8 M  $\text{LiBOB}$  EC/DEC had lower thermal reactivity with  $\text{Li}_{0.81}\text{C}_6$  but much higher thermal reactivity with  $\text{Li}_{0.5}\text{CoO}_2$  than pristine  $\text{LiPF}_6$ -based electrolytes [68,69]. Interestingly, 0.8 M  $\text{LiBOB}$  EC/DEC possessed lower thermal reactivity with charged  $\text{LiFePO}_4$  than pristine  $\text{LiPF}_6$ -based electrolytes, indicating graphite/ $\text{LiFePO}_4$  battery using 0.8 M  $\text{LiBOB}$  EC/DEC would be very abuse-tolerant [100]. From the perspective of lithium salts concentration, ARC results indicated that increasing the  $\text{LiPF}_6$  concentration in electrolyte (EC/DEC as solvents) could alleviate the combustion reaction between electrolyte and  $\text{Li}_{0.5}\text{CoO}_2$  [96]. Differently, the thermal reactivity between electrolyte and charged  $\text{LiMn}_2\text{O}_4$  increased as the  $\text{LiPF}_6$  concentration in electrolyte (EC/DEC as solvents) increased [97]. Another interesting conclusion from ARC was that, increasing the  $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}]\text{O}_2$  (NCA) electrode density enhanced the thermal reactivity between charged NCA and 1.0 M  $\text{LiPF}_6$  EC/DEC, because of the fact that a denser electrode contained less lithium salt of  $\text{LiPF}_6$  [102]. Flame retardant solvents/additives have been proposed to extinguish a fire when batteries get thermal runaway [18]. But, the effects of flame retardant solvents/additives on the thermal reactivity between charged electrodes and electrolyte are seldom considered. Using ARC, J. R. Dahn et al. revealed that the presence of TPP in electrolyte significantly increased the thermal reactivity between charged  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  and electrolyte (Fig. 2f) [71]. Another example showed that the addition of sulfolane co-solvent into carbonate electrolytes could suppress the

SHR between charged  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and electrolyte [103]. As for functional additives, in some cases, adding 10 wt% VC, FEC or vinyl ethylene carbonate (VEC) into 1.0 M  $\text{LiPF}_6$  EC/DEC did not significantly impact the thermal reactivity of charged  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  with electrolyte [73]. Interestingly, ARC results suggested that the thermal stability of charged  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  with electrolyte decreased slightly with the addition of additives (lithium bis(oxalato)borate ( $\text{LiBOB}$ ) and succinonitrile (SN)) but the thermal stability of charged NCA with electrolyte increased with the addition of the same additives [105]. These examples of formulating electrolytes tell us that we should keep a careful eye on the impact of lithium salts, solvents, and functional additives on the cathode/electrolyte thermal compatibility.

Undoubtedly, ARC can be used to compare the thermal safety of different cathode materials with electrolytes. For example of the high-profile nickel-manganese-cobalt layered oxides ( $\text{Li}[\text{Ni}_x\text{Mn}_y\text{Co}_z]\text{O}_2$ , x: y: z = 1: 1: 1 (NMC111), 4: 4: 2 (NMC442), 5: 3: 2 (NMC532), 6: 2: 2 (NMC622), 8: 1: 1 (NMC811)), ARC results showed that NMC811 was significantly more reactive (demonstrating higher SHR and lower onset temperatures for exothermic reactions) with electrolyte than the other NMC grades [115]. Except NMC811, as the upper cut-off potential of other NMC grades increased, the SHR between cathode and electrolyte increased, especially at 4.7 V, indicating a trade-off between high energy density and safety (Fig. 2g). Moreover, it was revealed that single crystal NMC532 (with electrolyte) was less reactive than standard polycrystalline NMC532 (with electrolyte), uncovering the role of electrode material morphology and synthesis methods in determining safety [116]. Interestingly, ARC results from D. D. MacNeil demonstrated that a series of charged  $\text{LiFePO}_4$  cathodes had, overall, a comparable thermal reactivity with electrolyte regardless of synthetic routes or specific surface area and that the thermal stability of the charged  $\text{LiFePO}_4$  cathodes with electrolyte was superior to that of charged  $\text{LiCoO}_2$  with electrolyte [131]. Doping Al element was far more effective than Mg element in enhancing the thermal stability between  $\text{LiCoO}_2$  and electrolyte [124]. Coating NCA cathode with  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  were able to significantly lower the thermal reaction between charged NCA and electrolyte [132]. Aforementioned reports will enlighten us to deeply and comprehensively understand the complicated battery safety issue from the perspective of battery materials.

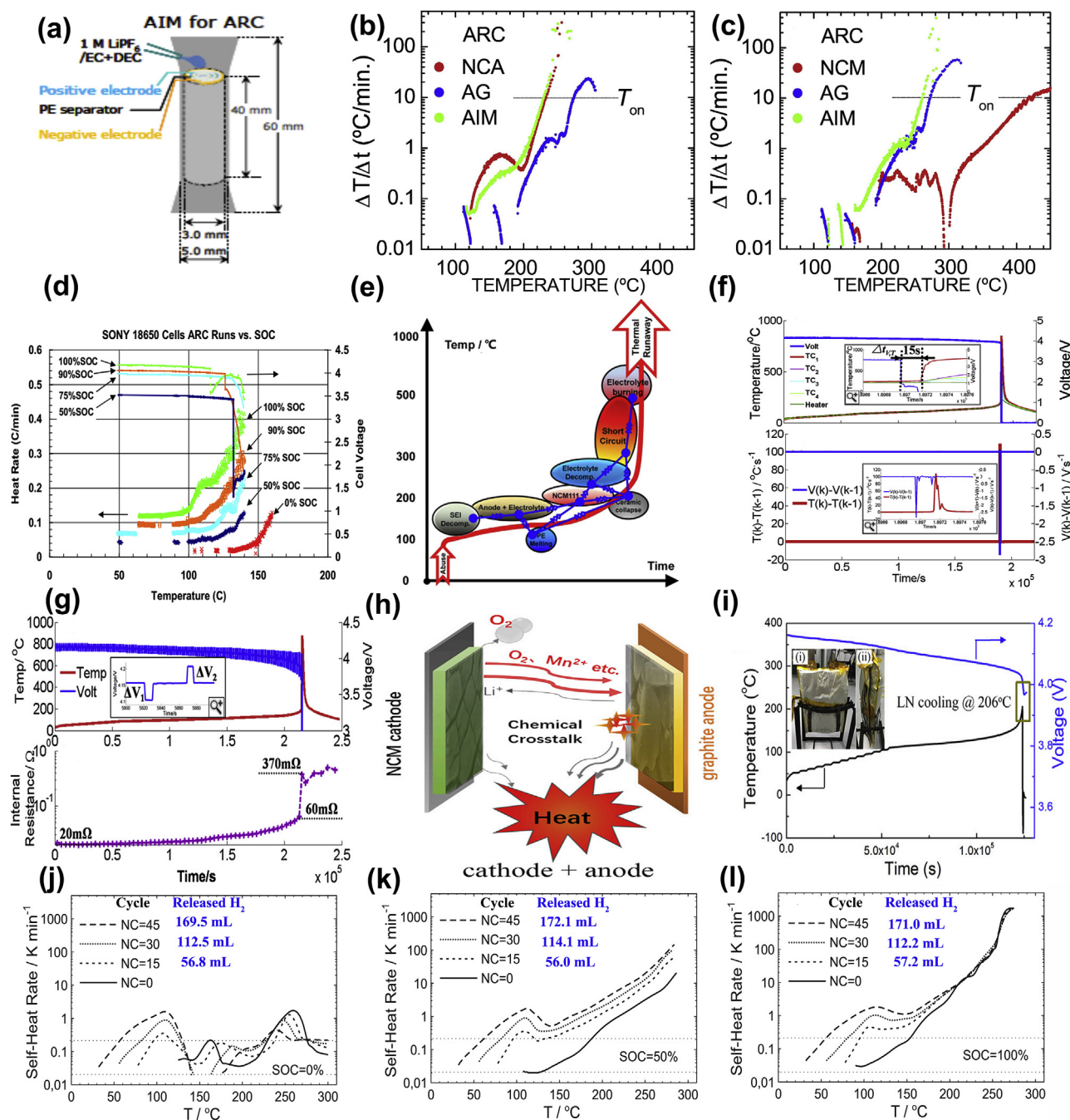
## 2.2. Battery single cell and pack evaluation by ARC

### 2.2.1. Thermal runaway features of battery single cell

The thermal runaway processes of LIBs are greatly associated with decomposition of solid electrolyte interface (SEI) layer, anode/electrolyte reactions, cathode/electrolyte reactions, self-decomposition of electrolyte, separator shrinkage/melt/combustion, etc. [13,14]. Therefore, as described above, one single factor, such as high thermal stability of electrolyte or separator, excellent anode/electrolyte thermal compatibility or cathode/electrolyte thermal compatibility does not guarantee the high safety of a battery single cell. In other words, presently, it is ignored but necessary to study the role of battery materials on safety at the scale level of a battery single cell by ARC, especially large format and large capacity cells. On the one side, electrolytes have been demonstrated to be a major source of poor safety response of LIBs, and their safety evaluation in full cell are very important but overlooked [14,136–141]. For example, overcharge protection additive of 4-bromobenzyl isocyanate (Br-BIC) could electrochemically polymerize at 5.5 V to stop thermal runaway of MCMB/ $\text{LiCoO}_2$  battery during overcharging processes [138]. However, ARC results showed that this 18,650-type full cells with Br-BIC additive experienced thermal runaway faster than the counterpart. For a 5 Ah NMC111/MCMB pouch cell, ARC investigations at Heat-Wait-Search (HWS) mode demonstrated that the addition of 5 wt% PFPN flame retardant into standard electrolyte significantly reduced the SHR in the temperature range from 80 °C to 110 °C [140]. On the other side, the roles of either anode or cathode materials on safety are also crucial [57,142–144]. ARC experiments conducted on 18,650-type

LiFePO<sub>4</sub>/graphite cells (0.85 Ah) suggested that the type of graphitic anode materials significantly affected the battery safety [57]. More importantly, both DSC (at material level) and ARC (at battery level) results confirm that the kinetics data from DSC at the graphite anode component level were a reliable indicator to judge the thermal stability of

large capacity full cells. By using an all-inclusive microcell (AIM, Fig. 3a) method, K. Mukai et al. performed ARC analyses on NCA/graphite and NMC111/graphite full cells, demonstrating that NCA governed the thermal runaway for the former cell (Fig. 3b), whereas graphite for the latter cell (Fig. 3c) [142]. It was validated in 5 Ah pouch cell that LiFePO<sub>4</sub>



**Fig. 3.** (a) Simple illustration of All-inclusive microcell (AIM) for ARC [142]. (b) SHR vs. temperature for NCA|LiPF<sub>6</sub>(EC/DEC), artificial graphite(AG)|LiPF<sub>6</sub>(EC/DEC), and NCA|LiPF<sub>6</sub>(EC/DEC)|AG. (c) SHR vs. temperature for NCA|LiPF<sub>6</sub>(EC/DEC), artificial graphite(AG)|LiPF<sub>6</sub>(EC/DEC), and NCA|LiPF<sub>6</sub>(EC/DEC)|AG. For (b) and (c), the thermal runaway onset temperature ( $T_{on}$ ) was defined as the temperature at which  $\Delta T/\Delta t \geq 10^\circ\text{C min}^{-1}$  [142]. (d) ARC data for commercial Sony Li-ion 18,650 cells (US18650S STG) from 0 to 100% SOC (vertically offset) showing onset of self-generated heating along with cell voltages [150]. (e) Qualitative interpretation of the thermal runaway chain reactions of a 25 Ah prismatic NCM/graphite battery [7]. (f) The time interval between the voltage drop and the temperature rise during thermal runaway ARC test of a 25 Ah prismatic NCM/graphite battery. (g) The variation of the internal resistance during the thermal runaway ARC test of a 25 Ah prismatic NCM/graphite battery [157]. (h) Illustration of proposed chemical crosstalk process between cathode and anode [24]. (i) Temperature and voltage curves of thermal runaway at 206 °C obtained by liquid nitrogen (LN) purge. Inset shows the front view (left) and side view (right) of the lithium-ion batteries after LN cooling. ARC Results for 18,650-type NCM/Graphite cells with number of charge/discharge cycles NC = 0, 15, 30 and 45 (at 0 °C), while the cells are charged to 0% SOC (j), 50% SOC (k) and 100% SOC (l). The dashed lines are indicative of the initial temperature of the exothermic reactions (at SHR = 0.02 K min<sup>-1</sup>) and the thermal runaway temperature at SHR = 0.2 K min<sup>-1</sup>. The corresponding released hydrogen were also marked [170].

coating on NMC532 (NMC532-LFP composites) not only improved the electrochemical performances but also significantly increased the temperature point of thermal runaway [144]. It is well known that the thermal stability of separator has great impacts on thermal safety of batteries [145–148]. Despite of their excellent electrochemical/chemical stability and high mechanical strength in machine direction (MD)/transverse direction (TD), the commercial and widely-used polyolefin microporous separators (such as polyethylene (PE, with a melting point of  $\text{ca.} 130^\circ\text{C}$ ) and polypropylene (PP, with a melting point of  $\text{ca.} 170^\circ\text{C}$ )) for LIBs always suffer from severe thermal-induced shrinkage, highly flammable and poor electrolyte wettability, inevitably causing safety concerns. Recent years, a variety of efforts have been devoted to develop separators (such as polyimide (PI) separator, cellulose separator, and ceramic-based composite separators, etc.) with high thermal stability and excellent flame retardancy. However, ARC experiments are seldom conducted to reveal the impact of varied newly-developed separators on thermal safety at battery cell level. In addition, it is necessary to point out that separators with high thermal stability and excellent flame retardancy do not guarantee the safety of the LIBs. For example, ARC experiments conducted on a large-format 25 Ah NMC532/graphite pouch cell using a PET/ceramic non-woven separator (PET nanofiber melting point  $\text{ca.} 257^\circ\text{C}$ ) revealed that battery thermal runaway was ignited by chemical crosstalk (between cathode and anode), not by heat generation from internal short circuit [24].

To guarantee the battery safety in practical application, it is necessary to reveal the thermal runaway features of any (any available type, any available size, and any available capacity) LIB under any state of charge (SOC) and state of health (SOH), by using ARC measurements [149–170]. For commercial Sony 18,650 cells, ARC results demonstrated that the self-heating onset temperature decreased with increasing SOC from 0% to 100%, while the magnitude of SHR increased at a given temperature (Fig. 3d) [150]. In addition, the “knee” in the SHR curve around  $110^\circ\text{C}$  was ascribed to heat releasing from the breakdown of SEI layer, while the “dip” in the SHR curve at  $125^\circ\text{C}$  was attributed to the endothermic melting of the polyethylene separator material (also indicated by the sudden drop of cell voltage). It is very important to clarify the role of the cathode and anode in heat generation during thermal runaway processes of LIBs. H. Maleki et al. interestingly found that, for a 750 mAh prismatic cell consisted of Sn-doped  $\text{LiCoO}_2$  cathode and meso-carbon micro-fiber (MCMF) anode, the total heat generating was dominated by cathode between 50% and 125% SOC, whereas anode dominated total heat generating when the SOC at the range of 125%–200% [151]. ARC test performed on 18,650-type  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  battery showed no thermal runaway, explosion, or fire [153]. Using ARC, M. Ouyang studied the thermal runaway features of a 25 Ah prismatic NCM/graphite battery, the qualitative interpretation of the chain reactions during thermal runaway was given by using ARC and DSC (Fig. 3e) [13,157]. When thermal runaway happened, the temperature inside the 25 Ah battery was  $870^\circ\text{C}$  or so, and the temperature difference within the battery was  $520^\circ\text{C}$ . More importantly, it was revealed that there was a time interval of 15–40 s from the sharp voltage drop to the instantaneous rise of battery temperature, benefiting for early warning of the battery thermal runaway (Fig. 3f). Additionally, the internal resistance of 25 Ah battery (got by pulse current charging) increased slowly from 20 m $\Omega$  to 60 m $\Omega$  before thermal runaway, while it rose to 370 m $\Omega$  when thermal runaway happened indicating the loss of the integrity of the separator or the battery swell (Fig. 3g). Very recently, it was demonstrated by M. Ouyang’s group that not only internal short circuiting, but also chemical crossover (cathode released oxygen was consumed by the lithiated anode, generating heat to trigger thermal runaway, Fig. 3h) was the mechanism behind thermal runaway of LIBs [24]. To confirm the unprecedentedly proposed chemical crossover mechanism, a 25 Ah battery undergoing the thermal runaway process in ARC equipment was quickly frozen by liquid nitrogen and it was subjected to detailed post-test analysis (Fig. 3i). Differently, by analyzing gas collected by ARC experiment, N. E. Galushkin proposed that released heat from recombination

of atomic hydrogen accumulated in anode graphite contributed to the initiation of thermal runaway in lithium-ion cells (Fig. 3j–l) [170]. It is noted here that ARC has the function of collecting generated gases after the battery thermal runaway. Actually, these generated gases during battery thermal runaway are toxic [171–178], and their components are greatly affected by different battery systems with different electrolytes (lithium salts, solvents, and additives), electrodes, and separators. Despite complicated and challenging, it is necessary to identify and reduce the toxic species for every commercial battery system during thermal runaway. In addition, depicting the generation paths for gases releasing is also very important. By using equipped digital camera, another function of ARC is to accurately judge the time and temperature when battery get smoke, fire or explosion. In summary, the real thermal runaway mechanisms of LIBs are much more complicated than the conclusions got before. Except the varied testing methods (including ARC) mentioned in Fig. 1a, we must do bulk electrode and electrode interface analysis by using *in-situ* or *ex-situ* analytical techniques [179], establishing the deep correlation between electrode (bulk electrode and electrode interface components/properties) and thermal runaway features of LIB, despite challenging. Moreover, the thermal runaway processes are obviously different for different LIB systems, and it is suggested that, for every LIB product operated at normal conditions, it is urgently needed to establish safety data base, containing thermal runaway features (including the toxic gases identification) at different state of charge (SOC) and state of health (SOH).

In practical applications, LIBs will inevitably suffer from mechanical (nail penetration, crush), thermal (high temperature storage, rapid thermal shock, subzero temperature usage) [150,158,161,170,180–188], electrical abuse conditions (short circuit, overcharge) [189–193], greatly increasing the safety risks. For mechanical abuse, ARC can be equipped with sections for nail penetration and crush test. Many thermocouples can be elaborately arranged on the surface or inside of the battery, detecting battery temperature distribution under abuse conditions. Thermal abuse is the most common condition in practical battery applications. For commercially available 2.2 Ah 18,650-type NMC532/graphite batteries charged and discharged at  $0^\circ\text{C}$  until the SOH = 70%, exothermic reactions shifted below  $50^\circ\text{C}$  and became very strong, showing no SOC dependency [161]. The increased thermal runaway risk at low temperatures is proposed to be greatly associated with the growth of high surface area dendritic lithium metal on graphite [161,170,181–183]. When aged at  $45^\circ\text{C}$  compared to  $20^\circ\text{C}$ , 2.2 Ah 18,650-type NMC532/graphite batteries showed higher onset temperature for self-heating because of the formation of an effective and thermally stable SEI at graphite anode (without the presence of metallic lithium deposits compared to  $20^\circ\text{C}$ ) [184]. By using ARC, M. Ouyang validated an electrochemical-thermal coupled overcharge-to-thermal-runaway (TR) model to predict the highly interactive electrochemical and thermal behaviors of lithium ion battery under the overcharge conditions [191]. For every LIB product operated at abuse conditions, it is also urgently to clarify the thermal runaway mechanisms, and establish safety data base containing all detailed thermal runaway features. Overall, it is believed that these ARC-derived strategies and perspectives will enlighten us to develop safer battery products.

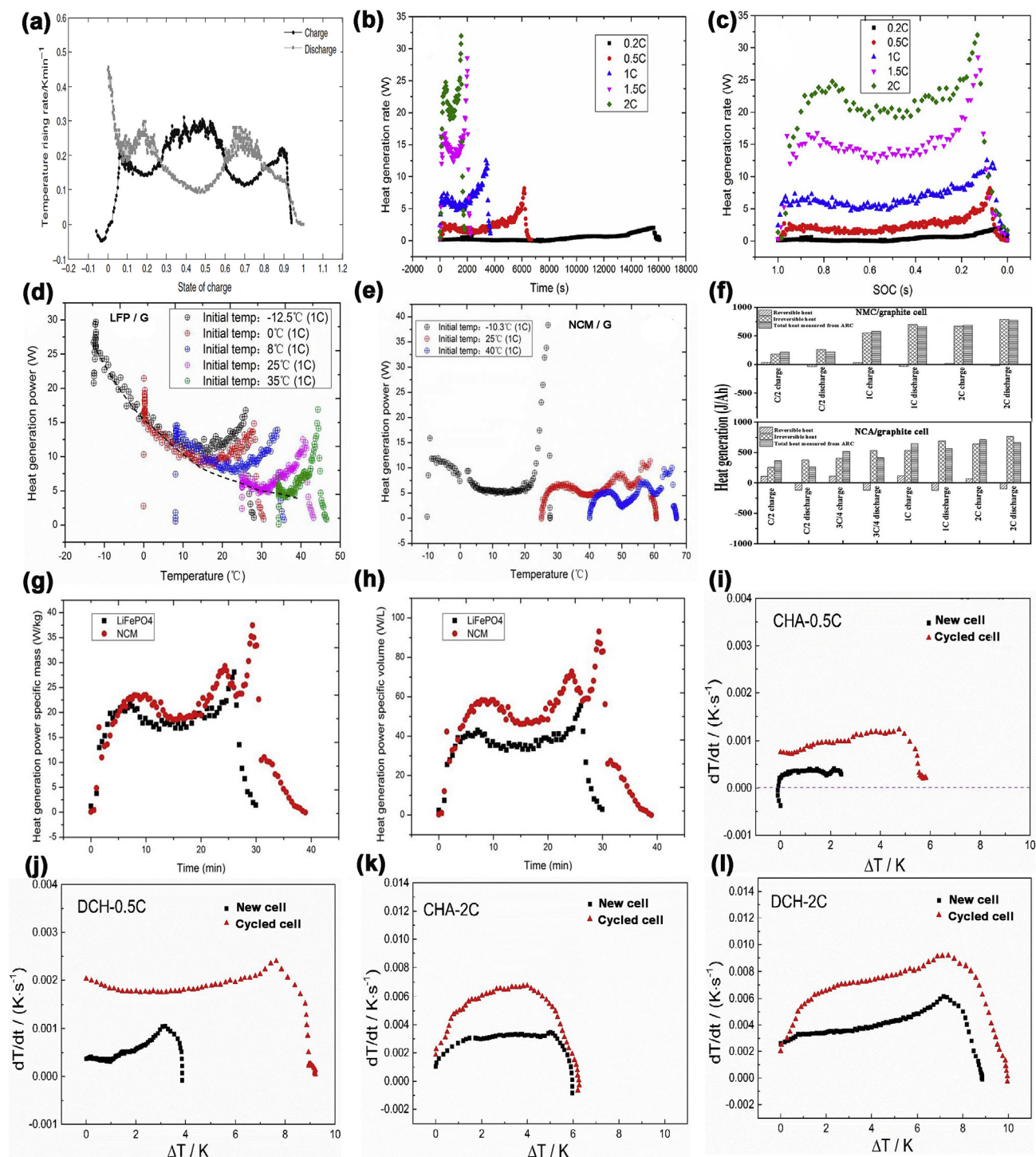
## 2.2.2. Heat generation determination by ARC

It is vital and essential to design a reliable battery management system (BMS) that enables a battery pack to work in an ideal controlled temperature range. A precise determination of heat generation in batteries are crucial for battery pack BMS designing [17,194–209]. Heat generation processes inside batteries are very complex, requiring understanding of how the electrochemical reaction rates change with time and temperature, and how current is distributed within large format batteries [17]. In general, the heat generation broadly includes reversible and irreversible heat generation. The reversible heat generation is a measure of entropic coefficient of the cell which depends on the intrinsic nature of the electrode materials (relating with the atom arrangement in



the crystal lattice of the electrode materials). On the other hand, the polarization or overpotential of the cell during operating induces ohmic heat, constituting the irreversible heat. In other words, the irreversible heat generation arises from internal resistance, depending on a number of cell components (electrodes, electrolyte, current collector, separator, etc.) [205]. Many approaches have been developed to estimate heat

generation, for example, potentiometric and calorimetric ways for reversible heat determination, and the intermittent pulse technique, electrochemical impedance spectroscopy (EIS) and newly developed energy method for irreversible heat investigation [13,196,197,199,205]. Among them, ARC is one of the most effective tools for studying the temperature changes and heat generating rate due to the adiabatic



**Fig. 4.** (a) The average temperature rising rate of a 25 Ah large format cell during charge/discharge at 1 C rate in ARC [197]. Heat generation rates during discharging vs time (b) and SOC (c) at different current rates with an initial temperature of 25 °C [207]. The heat generation map of the LFP/G (d) and NCM/G (e) batteries at various operating temperatures [204]. (f) Heat generation of 18,650-type  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2/\text{graphite}$  (NMC/graphite, top) and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2/\text{graphite}$  (NCA/graphite, bottom) cell at 35 °C operating temperature in ARC [205]. Comparison on the specific mass (g) and specific volume (h) heat generation power of the LFP/G and NCM/G battery cells at an initial temperature of 25 °C during 1 C-rate discharge [204]. (f) Temperature rise rates of fresh and 2100 times cycled cells during charge at 0.5C (i), discharge at 0.5C (j), charge at 1 C (k) and discharge at 1 C (l) [206].



environment feature, and could be available for any LIB during charging and discharging. In ARC, the total heat generation rate ( $Q$ , W) is determined by the following equation:  $Q = m \cdot C_p \cdot dT/dt$ , where  $m$  (g) is the battery mass,  $C_p$  ( $J g^{-1} K^{-1}$ ) is the specific heat capacity of the cell determined by ARC  $C_p$  test, and  $dT/dt$  ( $K s^{-1}$ ) is the temperature rising rate measured by the attached feedback thermocouples on the surface of the cell during the charge/discharge cycling processes [13,196,197,199,205,206]. As for the  $C_p$  test, it is conducted by using “mCp” mode of ARC, and  $C_p$  ( $J g^{-1} K^{-1}$ ) was calculated according to the following equation:

$$P = Q_c / \Delta t_c = m C_p \Delta T / \Delta t_c$$

Where  $P$  (a constant parameter, about  $0.88 J s^{-1}$ ) and  $Q_c$  (J) is the heating power and provided heat by ARC, respectively;  $\Delta t_c$  (s) and  $\Delta T$  (K) is the heating time and adiabatic temperature increase, respectively;  $m$  (g) represents the mass of battery [206]. By connecting the ARC with a charge/discharge device, the entropy coefficient could be determined by  $(Q_{charge} - Q_{discharge}) / 2IT$ , and thus reversible heat could be calculated by:  $Q_{rev} = (Q_{charge} - Q_{discharge}) / 2$ , where the  $Q_{charge}$  and  $Q_{discharge}$  are the total heat generation rate obtained by ARC during charge and discharge,  $I$  is the current amplitude and  $T$  is the cycling temperature [197]. In this calorimetric method, under the same current amplitude  $I$ , the irreversible heat generation rate during charge and discharge was assumed to be identical. In a more accurate way [206], the irreversible specific heat generation rate  $q_i$  ( $J s^{-1} g^{-1}$ ) is calculated according to the following equation:

$$q_i = I^2 R_o / m + I \eta / m = I^2 (R_o + R_p) / m = I^2 R / m$$

Where  $I$  (A) is working current,  $R_o$  ( $\Omega$ ) is ohmic resistance,  $m$  (g) is battery mass,  $\eta$  (V) is over potential,  $R_p$  ( $\Omega$ ) is polarization resistance,  $R$  ( $\Omega$ ) represents total internal resistance. The ohmic resistance and total internal resistance of the battery are always studied by using the method of hybrid pulse power characterization (HPPC) on the battery test system. The reversible specific heat generation rate  $q_r$  ( $J s^{-1} g^{-1}$ ) is calculated according to the following equation:

$$q_r = Q_r / m \Delta t = T \Delta S / m \Delta t = (\partial E_{ocv} / \partial T)_p T z F / m \Delta t$$

Where  $\Delta t$  (s) is charge or discharge time,  $T$  (K) is battery temperature,  $\Delta S$  ( $J mol^{-1} K^{-1}$ ) is entropy change of reversible chemical reactions,  $z$  (mol) is electron number transferred by electrode reaction,  $F$  is Faraday constant, and  $(\partial E_{ocv} / \partial T)_p$  ( $V K^{-1}$ ) is entropy coefficient.

J. Zhang et al. investigated temperature rising rates of the NCM/C pouch cell and revealed that the heat generation rates of charge and discharge are almost symmetrical as expected (Fig. 4a), and the calculated entropy coefficient as well as the heat generation values were in good agreement with those obtained by other approaches [197]. C. Lin et al. concluded from ARC results that during charge/discharge process at low current rates, the temperature increase in LIBs is predominantly attributed to the entropy changes in electrode materials. When rising the current rates, augments of cell heat generation in both magnitude and volatility were observed, due to the released heat depending more on the internal resistance rather than the cathode/anode material systems (Fig. 4b–c) [207]. In addition, they also revealed that lower initial cycling temperatures led to higher heat generation rate, which was caused by the big internal resistance (Fig. 4d–e) [204]. Efforts have also been made to elucidate the influence of electrodes materials on the thermal behavior of LIBs using ARC. Different heat generation behavior among the NCM/G, LFP/G, and NCA/G batteries was than that from the Ni-rich NMC one because of the higher phase change [205]. It is also worth noting, different heat generation behavior among the NCM/G, LFP/G, and NCA/G batteries was observed, and NCM cathode battery presented the highest specific heat generation (Fig. 4f–h) [204,205]. For NCM/G system, Co-rich NMC cell was found to produce larger heat generation. The cycling aged LTO LIBs exhibited much higher heat generation rate as well

as the heat capacity, at all C-rates, than those of the fresh one (Fig. 4i–l). And more reversible heat during charging process was released for the cycled battery, demonstrating that more attention should be paid on monitoring and controlling the thermal behavior of the aged batteries [206].

### 2.2.3. Thermal runaway study of battery pack

By connecting amounts of battery single cells in series and/or in parallel, battery packs with large capacity and high working voltage are produced to provide the necessary power for xEVs and ESSs. Due to the different heat dissipation and electric connections, the thermal safety behaviors of the cells in a pack are different from those of a single battery cell. At present, varied modeling approaches have been developed to investigate thermal safety of LIBs, at levels of material, cell, and pack [18,198,200,210–219]. Modeling at battery pack level can help us to understand the risks of propagation of a single battery cell thermal runaway within a battery pack, serving to confine the damage to the environment of the failing cell and prevent further destruction or disability in the pack [18,211,212,214,215,217–219]. By using SHR given by ARC, Robert M. Spotnitz described a simple approach to simulate the thermal abuse resistance of a 8-cell (18,650-type) battery pack when one cell went into thermal runaway [211]. It was revealed that pack thermal runaway propagation could occur depending on the ability of the neighboring cells to dissipate and absorb heat. Using ARC results as criteria, M. Ouyang group proposed several thermal models to predict and prevent thermal runaway propagation when one single large format battery cell in a battery pack was nail penetrated to thermal runaway [212,214,215,219]. It was concluded that the heat transferred through the battery shell dominated the heat transfer process, while fire contributed little during a penetration-induced thermal runaway propagation of a battery pack. In subsequent, several strategies like raising thermal runaway triggering temperature, reducing the total electric energy released, enhancing the heat dissipation coefficient, and adding extra thermal resistant layers between adjacent batteries were suggested to delay or prevent the thermal runaway of a battery pack. Recently, it was revealed that graphite composite sheet and Al extrusion as interstitial materials could effectively suppress thermal runaway propagation in a battery pack containing commercial 18,650 cylindrical cells [217].

## 3. Thermal safety evaluation of battery chemistries “beyond Li-ion” by ARC

In the name of lower cost, “better safety”, higher energy density or higher power density, varied energy storage devices “beyond conventional Li-ion battery”, such as lithium metal based batteries [8–11,25,220,221], sodium based batteries [56,70,222–236], multivalent secondary batteries (such as magnesium, calcium, aluminum, and zinc based batteries) [236–239], dual-ion batteries [236,240–242], capacitors [243], etc. have been arousing great interests in recent years. Encouragingly, huge amounts of papers focusing on enhancement of electrochemical performances or background scientific mechanisms have been published to facilitate the evolution of these burgeoning energy storage devices. Unfortunately, the thermal safety issues of these burgeoning energy storage devices are seldom focused, either at the material level or at the single battery cell level. This is very strange, because the thermal safety issues must be systematically evaluated from the point of both commercial practical applications and basic research. Conducting ARC experiments is suggested to evaluate the thermal safety of these burgeoning energy storage devices, just as abovementioned examples for LIBs.

In specific, there are few reports about the application of ARC in evaluating the thermal safety of lithium metal based batteries [25,220,221]. Recently, blended-salts electrolytes have achieved great progress in the field of lithium metal batteries [25,91,244]. Using ARC, Hong Li et al. revealed that 2 Ah pouch-type lithium metal batteries using LiTFSI–LiDFOB–LiPF<sub>6</sub> based blended-salts electrolyte systems were safer than

those batteries using traditional  $\text{LiPF}_6$  based electrolyte [25]. This is the first example to study the thermal safety issue of large format lithium metal batteries using liquid electrolytes by using ARC. Earlier, ARC experiments suggested that pouch type solid state lithium metal battery ( $\text{Li}/\text{LiFePO}_4$ ) using solid polymer electrolyte ( $\text{LiTFSI}$ -polyether composites) were demonstrated to possess much higher thermal stability than pouch type lithium metal battery ( $\text{Li}/\text{LiFePO}_4$ ) using conventional  $\text{LiPF}_6$ -carbonates based liquid electrolyte [220]. As for lithium sulfur batteries, cell with sulfur- $\text{LiV}_3\text{O}_8$  composite cathode was found to have the highest onset temperature for thermal runaway and also the lowest maximum SHR [221]. As for sodium based batteries, ARC evaluation is also seldom conducted [56,70,227–235]. From the perspective of anode/electrolyte or cathode electrode thermal compatibility, J. R. Dahn's group have conducted some ARC experiments to understand the thermal stability of sodium ion batteries [70,227–231]. Moreover, preliminary ARC results suggested that large format sodium ion batteries are safer than LIBs [56,233]. In summary, thermal safety evaluation by ARC experiments on burgeoning energy storage devices are definitely still lacking, and their road to real applications remains very long.

#### 4. Summary and outlook

In summary, the highly-integrated ARC technology plays a crucial in evaluating the thermal safety of LIBs and varied energy storage devices “beyond Li-ion”, at multilevel of material, single cell, and pack. The aforementioned ARC experiments on LIBs will help us to systematically and comprehensively understand the complicated battery safety issue, also contribute to the safety enhancement of batteries. In the following, we will give a summary and provide critical perspectives to facilitate thermal safety study and improvement of batteries:

**A.** ARC experiments can be conducted to evaluate the thermal stability of electrode, electrolyte, and electrode/electrolyte, clarifying the key role of electrode engineering (material type, SOC of material, material morphology, material surface coating, material bulk doping, material synthesis route, electrode binder, etc.) and electrolyte formulation (lithium salt, solvent, functional additive), etc., on battery safety.

In specific, it is noted that improving thermal stability of electrolyte or/and enhancing anode/electrolyte thermal compatibility sometimes not mean or ensure the safety enhancement of corresponding large format cells, due to the undesired higher thermal reactivity between cathode and electrolyte. For example, the adoption of some thermally stable lithium salts in electrolyte not always bring the improvement of cathode/electrolyte thermal compatibility, and the inherent scientific mechanisms are still needed to be clearly depicted. It is suggested here that much more considerations must be given to clarify the physical and health hazards of the gas byproducts generated during electrolyte combustion, especially when some flame retardant co-solvents are used in electrolyte. Moreover, it seems like that the flame retardant ability of electrolyte is excessively emphasized, and it is always unclear that whether the flame retardant electrolyte will make the thermal stability of the battery worse nor better. As for electrode materials, in the process of searching novel high capacity anode materials (such as LTO, Si-based materials, conversion-type anodes, etc.) or high capacity/high voltage materials (such as  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , lithium-rich layered oxides, nickel-rich layered oxides, etc.), one-sided pursuit of electrochemical performances is focused, more emphasis on their thermal reactivity with varied electrolyte and safety evaluation on large format cells are urgently needed from the point of real applications.

**B.** ARC experiments can be conducted to reveal the thermal runaway features of any (any available type, any available size, and any available capacity) LIB under any state of charge (SOC) and state of health (SOH). Presently, it is ignored but necessary to use ARC to study the role of battery materials (electrode material, electrolyte, separator, etc.) on safety at the scale level of a battery single cell, especially large format and large capacity cells. Up to date, the real thermal runaway mechanisms of LIBs are much more complicated than the conclusions got before. Except

the varied testing methods (including ARC) mentioned in Fig. 1a, we must do bulk electrode and electrode interface analysis by using *in-situ* or *ex-situ* analytical techniques [179], establishing the deep correlation between electrode (bulk electrode and electrode/electrolyte interface components/properties) and thermal runaway features of lithium ion battery, despite challenging. Moreover, the thermal runaway processes are obviously different for varied lithium ion battery systems, and it is suggested that, for every commercial LIB product operated at both normal and abuse conditions, it is urgently needed to establish safety data base, containing thermal runaway features (including the toxic gases identification) at different state of charge (SOC) and state of health (SOH). In addition, even though the ARC test provides informative information on the thermal features of batteries in normal and abused conditions, the inherent chemical reactions as well as the gas production processes at elevated temperatures are still unrevealed. Synergetic approaches of ARC with other characterizations, such as simultaneous thermal analysis (STA), gas chromatography mass spectrometry (GC-MS), liquid chromatography mass spectrometry (LC-MS), *in-situ* XRD, and *in-situ* FTIR etc., should be developed for further depicting the detailed mechanisms rooted in the thermal runaway process. Overall, it is pointed out that establishing battery safety industry standard based on ARC results is very important, and it is believed that these ARC-derived strategies and perspectives will enlighten us to develop safer battery products.

**C.** ARC experiments can be used to identify the  $C_p$  and heat generating rate, which are vital and essential for designing a reliable battery pack BMS. In addition, ARC results can be used as criteria to study the thermal runaway propagation model when one single large format battery cell in a battery pack gets thermal runaway.

**D.** In the name of lower cost, “better safety”, higher energy density or higher power density, varied energy storage devices “beyond conventional Li-ion battery” (lithium metal based batteries, sodium based batteries, multivalent secondary batteries, dual-ion batteries, capacitors, etc.), have been arousing great interests in recent years. Unfortunately, the thermal safety issues of these burgeoning energy storage devices are seldom focused, either at the material level or at the single battery cell level. ARC experiments are suggested to evaluate the thermal safety, from the point of both commercial practical applications and fundamental research, of these burgeoning energy storage devices, just as above-mentioned examples for LIBs.

**E.** For practical application, thermal runaway mitigating strategies at multilevel of material, cell, and pack are necessary to improve the overall safety. A very recent review by M. G Ouyang summarizes the mitigation strategies for the thermal runaway of LIBs and provides insightful directions for guaranteeing the safety of LIBs [15]. Finally, it is pointed out that battery is a type of energy storage device (higher energy density, less safety), therefore, there is no absolute battery safety, only relative battery safety.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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