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TOPICAL REVIEW — Advanced calculation & characterization of energy storage materials & devices at multiple scale

Failure analysis with a focus on thermal aspect towards developing safer Na-ion batteries*

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Safety requirements stimulate Na-based batteries to evolve from high-temperature Na–S batteries to room-temperature Na-ion batteries (NIBs). Even so, NIBs may still cause thermal runaway due to the external unexpected accidents and internal high activity of electrodes or electrolytes, which has not been comprehensively summarized yet. In this review, we summarize the significant advances about the failure mechanisms and related strategies to build safer NIBs from the selection of electrodes, electrolytes and the construction of electrode/electrolyte interfaces. Considering the safety risk, the thermal behaviors are emphasized which will deepen the understanding of thermal stability of different NIBs and accelerate the exploitation of safe NIBs.

Keywords: Na-ion batteries, safety issue, electrodes, electrolytes, solid electrolyte interphase, thermal runaway, failure analysis

PACS: 65.40.–b, 65.20.–w, 65.40.gk, 88.80.ff **DOI:** 10.1088/1674-1056/ab7906

1. Introduction

In order to satisfy the growing demand of grid energy storage systems, the development of low-cost and long-life batteries is being accelerated. Na-ion batteries (NIBs), almost simultaneously developed with mature Li-ion batteries (LIBs), are attractive alternatives to LIBs because the earth-abundant sodium element can work as the charge carrier in NIBs.[1–3] With the rapid development of electrode and electrolyte materials, the energy density of NIBs has experienced great improvement which was previously regarded as one of the main challenges for the practical application.[4–6] However, for stationary energy storage systems which are usually constructed in rural area with a long-running operation, the safety property is of the primary concern.

Throughout the history of Na-based batteries, sodium–sulfur and sodium–metal halide battery technologies have been demonstrated for the power station in the last century.[7] However, their operation temperature is relatively high (about 300 °C), let alone the metallic sodium also easily catches fire in wet conditions, which suggests a serious safety vulnerability. Thus, the potential explosion risk of these high-temperature Na-based batteries prompts the evolution towards the room-temperature stationary NIBs, which are based on rocking-chair battery design with Na^+-host electrode materials. But the safety issue is easily overlooked and the challenges of building safer NIBs still exist. For example, compared with the Li^+ case, the larger (Shannon effective ionic radius) and heavier Na^+ suffers a poorer kinetics performance in host structures with insertion reaction mechanisms, thus the host matrix may degrade rapidly companied by an exothermic reaction. Besides, a higher solubility of the solid electrolyte interphase (SEI) was reported for NIBs due to the lower Lewis acidity of Na-complex, suggesting an incomplete protection of electrodes which may further induce the heat production.[8]

In this review, a summary about the failure and safety issue of NIBs is present considering new progresses achieved based on experimental results. We focus on strategies about how to build a safer NIB from the selection of electrodes and electrolytes. Moreover, the failure mechanisms of NIBs which are helpful to guide the safe battery design are discussed. Considering the main safety risk, the thermal behaviors (thermal stability) are emphasized, although electrochemical stability, mechanical stability, etc. are also important aspects for the failures of NIBs. Most importantly, we also include our own

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insights in this critical review.

2. Safety hazards and assessment

Similar to the case of LIBs, the origin of the safety problems lies in thermal runaway induced by heat release inside the battery or external damage. As shown in Fig. 1(a), the process of thermal runaway usually consists of the following three steps:[9] (1) the abnormal overheating, overcharge, short circuit, external impact, etc. induce the temperature of the batteries to increase towards a higher value; (2) an abnormal rise of battery temperature triggers the decomposition of SEI or electrolyte and the damage of the electrode crystal structure (especially cathode side), which bring more serious exothermic chain reactions with flammable gases (O_2, etc.) release; (3) the above reactions rapidly propagate and spread to the whole system, causing a sharp increase of temperature and pressure inside the battery, i.e., thermal runaway. Due to the highly active organic electrolytes, the final combustion and explosion are almost inevitable, which continue to damage the adjacent batteries, a disaster for NIBs with series–parallel connections for grid storage.

A safe NIB needs to go through the strict safety assessments based on the simulation of the above conditions. The effective safety assessments include safety testing (overcharge/discharge, external short-circuit, high temperature aging, etc.) and abuse testing (crush tests, nail penetration, fire, etc.). Moreover, the analysis results of pouch cells are more credible than that of coin cells. Taking the 2 A·h pouch cell of $Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$//pyrolyzed anthracite as an example, several tests are conducted on the fully charged pouch cells and the corresponding results are shown in Figs. 1(b)–1(e).[10] Firstly, the fully charged pouch cell with direct short circuit shows no smoke or fire. The temperature rises due to the instantaneous release of electric energy, and the elevated temperature causes the electrolyte decomposition which further leads to gas expansion (Figs. 1(b) and 1(e)). Then a battery overcharge test shows that a high voltage induces an electrolyte decomposition without obvious temperature increase (Figs. 1(c) and 1(e)). The final nail penetration test reveals that no smoke and fire are observed and the cell voltage can return to its normal value with pulling out the nail (Figs. 1(d) and 1(e)). In a broad sense, the safety requirements also involve nontoxicity which reminds a selection of non-toxic elements for the components of the battery. Besides specifying the safety requirements, the failure modes and related design strategies towards building safer NIBs are the key, which include the selection of electrodes, electrolytes, etc.

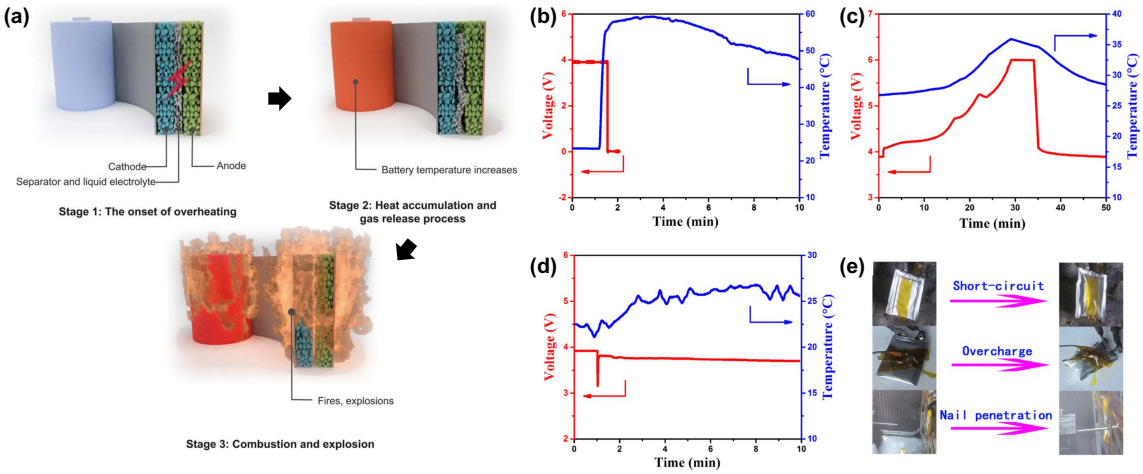


Fig. 1. (a) Three stages of the thermal runaway process.[9] (b)–(e) The safety test results of the prototype pouch cells ($Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$//pyrolyzed anthracite) at fully charged state. The voltage and temperature evolutions in the processes of (b) external short-circuit test, (c) overcharge test, and (d) nail penetration test; (e) the photographs of pouch cells before and after safety tests.[10]

3. The analysis towards electrodes

Intrinsic high safety is expected for electrodes of NIBs. For the cathode side, a stable crystal structure of cathode materials is vital as the decomposition of the active material at high voltage is a potential safety risk. The thermal stability of a typical layered cathode material $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ was measured with accelerating rate calorimetry (ARC).[11] As shown in Fig. 2(a), it was found that the onset temperature of exothermic reaction induced by the decomposition of the SEI is about 166 °C (T1). After a rapid exothermal acceleration, the battery temperature rises from 243 °C (T2, the onset of thermal runway) to the peak value (312 °C, T3). Further high-energy x-ray diffraction (XRD) analysis revealed that the thermal decomposition pathway of $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ structure at charged state is influenced by the external environment such as electrolyte and temperature, as shown in Fig. 2(b). It reminded us to avoid using NIBs in the highly reductive/oxidative environment (next section). Another layered $NaCrO_2$ was also evalu-

ated via ARC and it was found that $Na_{0.5}CrO_2$ (fully charged state) has no obvious reactivity until 350 °C.[12] However, in the lithium case, $Li_{0.5}CoO_2$ and even Li_0FePO_4 present an exothermic behavior below 300 °C. Further thermogravimetric analysis (TGA) and XRD confirmed that this high safety originates from little structural oxygen loss at the fully charged state. In fact, low oxygen activity is the intrinsic characteristics of some polyanionic cathode materials. Compared with the complex structural change in layered oxides with relatively easy oxygen evolution, polyanionic cathodes deliver highly reversible Na^+ insertion reaction under high temperature work conditions due to the thermodynamically stable intermediate products.[13] For example, $Na_2FeP_2O_7$ shows no oxygen evolution until 600 °C (Fig. 2(c)) and only suffers an irreversible phase transition (Fig. 2(d)), suggesting its high thermal stability induced by the stable pyrophosphate anion.[14]

Besides the selection of intrinsic high safe cathodes related to the crystal structure, interfacial reaction and related surface tuning also need to pay attention to. Surface/interfacial reactions easily trigger heterogeneous surface reconstruction accompanied with transition metal reduction (dissolution) and surface oxygen loss, which indicate an unstable cathode–electrolyte interphase (CEI) with the possibility of CEI fracture during long-term cycling or high temperature operation, as shown in Fig. 2(e).[15] Thus surface coating or doping is considered as the effective means to avoid the decomposition of CEI (the consideration about electrolyte will be discussed in the next section). Typically, Yu *et al.* designed a surface conducting carbon layer derived from pitch for the above-mentioned $NaCrO_2$ materials.[16] It was found from differential scanning calorimeter (DSC) and XRD results that this carbon coating can suppress the exothermic reaction from oxygen evolution, as shown in Fig. 2(f). Furthermore, a novel surface titanium doping for the manganese-based oxide cathode was reported to produce a protection layer of spinel-like titanium oxides and the mitigated manganese dissolution can reduce the heat generation at higher temperature.[17]

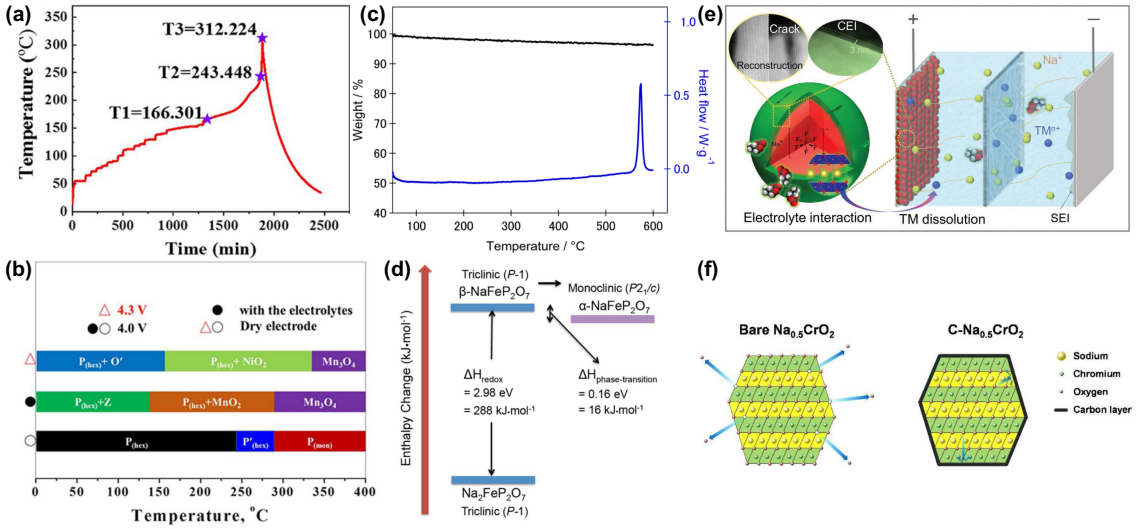


Fig. 2. (a) Temperature vs. time plot of the charged $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$/hard carbon full cell under thermal stability testing with ARC. (b) Schematic representation summarizing thermal decomposition process of charged $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ with different condition depending on the temperatures.[11] (c) Thermal analysis (TG-DSC) curves of the desodiated state $NaFeP_2O_7$ under steady Ar flow. (d) Enthalpy diagram of $Na_{2-x}FeP_2O_7$ polymorphs.[14] (e) Schematic summary of cathode–electrolyte interfacial chemistry induced battery degradation mechanism.[15] (f) Thermal mechanism of de-sodiated $Na_{0.5}CrO_2$ at high temperature.[16]

As for the anode side, the safety problem is more serious because it suffers from the SEI instability and Na metal plating risk at low voltage. On the one hand, it is difficult to directly use Na metal as anode considering its high reactivity and risk of explosion (unless using some solid electrolytes or other safe electrolytes). On the other hand, even without Na metal as anode it is still possible that the deposition of metallic Na happens in the entire battery system due to unmatched mass ratio of anode and cathode materials as well as inappropriate operation like overcharge (Fig. 3(a)).[18] Thus it is significant that the areal capacities of cathode and anode match each other during the cell design. In order to obtain a high energy density NIB, the anode with more low-voltage capacity (in half cell) may be a good choice. However, if the voltage is too low, Na metal plating may occur. For example, hard carbon anodes normally possess a typical sloping and plateau region in the potential profile, where the plateau region can contribute higher energy density in full cells but easily suffers from the Na metal plating (similar reaction voltage) at high current densities or low temperatures.[19,20] Under this circumstance, Qi *et al.* developed a low-temperature carbonization strategy to prepare a slope-dominated pitch-derived carbon anode with

satisfactory capacity and rate capability (Fig. 3(b)).[21] Most importantly, this slope-dominated carbon anode can enhance the ability to withstand the polarization to avoid the risk of Na deposition. Similarly, graphite anode (co-intercalation reaction), alloy anode, and others with moderate Na insertion potential (0.3–0.8 V in half cell) have their intrinsic advantages to withstand Na plating.[22]

In addition, at elevated temperatures, the sodiated anode (charging state in full-cells) will undergo a more violent reaction with electrolyte compared to the cathode due to the poor thermal stability of SEI formed on the anode surface. Zhao *et al.* assessed the thermal behaviors of a typical hard carbon electrode working with carbonate electrolytes and made a comparison between LIBs and NIBs.[23] It was found that sodiated hard carbon exhibited less exothermic heat generation and higher onset decomposition temperature than lithiated hard carbon, indicating a better thermal stability of NIBs, as shown in Fig. 3(c). Note that different electrolyte systems often trigger different thermal behaviors.[24,25] Disordered carbon usually delivers a less heat generation compared with the common graphite anode in LIBs because of the reduced reactivity related to the sp^3 carbon.[20] Moreover, the thermal properties of alloy materials are critical considering the high-energy density anode. A detailed DSC analysis revealed that sodiated tin (Sn) materials generate more exothermic heat compared to the lithiated tin materials, which is induced by an instable and thick SEI layer in NIBs, as shown in Fig. 3(d).[26] Thus carbonaceous electrodes may be a better anode choice considering cost and safety through comparing the enthalpies.[25,26]

Recently, a novel symmetric battery design using the same materials for both cathode and anode with high safety and production convenience emerges. For example, Wang *et al.* designed a cation-disordered electrode $Na_{0.6}Cr_{0.6}Ti_{0.4}O_2$ with long sloping charge/discharge curves (Fig. 3(e)).[27] Apart from the good rate performance, its moderate sodium insertion voltage (about 0.7 V) at the anode side also reduces the Na plating risk. The fabricated symmetric battery based on $Na_{0.6}Cr_{0.6}Ti_{0.4}O_2$ exhibits a safe sodium storage behavior with long cycle life at high current density. Besides the oxide materials,[28,29] some thermodynamically stable polyanionic materials are worth assembling into symmetric batteries in the future.[30]

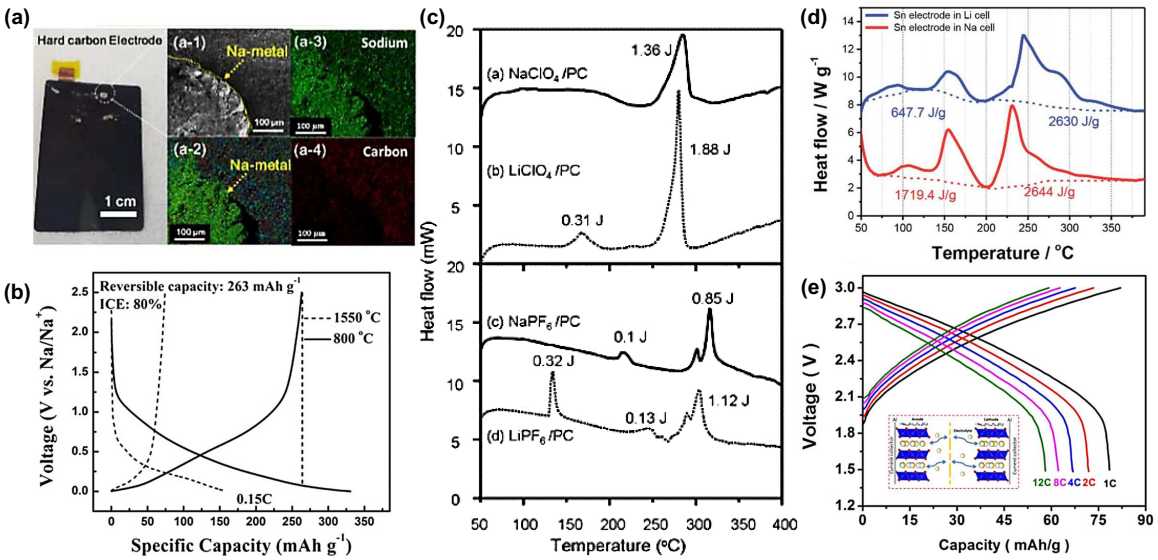


Fig. 3. (a) Digital photograph of hard carbon electrode collected from bare coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$/hard carbon full cell. (a-1) Scanning electron microscope (SEM) image and (a-2)–(a-4) corresponding energy dispersive x-ray spectroscopy mappings of the white circle region in (a).[18] (b) Comparison of the first discharge/charge curves of pitch-carbon-800 and pitch-carbon-1550 in half cells.[21] (c) DSC curves of 1 mg charged hard carbon electrode mixed with 2 ml EC/DMC (1 : 1 vol.%) solution containing 1 mol/dm^3 $NaClO_4$, $LiClO_4$, $NaPF_6$, or $LiPF_6$.[23] (d) DSC profiles of the lithiated (using $LiPF_6$ salt) and sodiated (using $NaPF_6$ salt) tin electrodes after three cycles.[26] (e) Discharge profiles of $Na_{0.6}Cr_{0.6}Ti_{0.4}O_2$/$Na_{0.6}Cr_{0.6}Ti_{0.4}O_2$ sodium-ion full cell at various rates.[27]

4. The analysis towards electrolytes

In traditional NIBs, the flammable organic liquid electrolyte is the "short board" of safety in the whole battery. Thus more consideration from the electrolyte side can greatly help to build a safer NIB. Most of the organic liquid electrolytes used in NIBs are referenced from LIBs. But Na salts usually show better thermal stability than Li salts due to higher electrostatic energy in ionic crystals of salts (Magdelung energy).[31] As for solvents, the cyclic solvent molecules exhibit higher onset decomposition temperature than that of linear one and co-solvents can reduce the heat release to some extent, as shown in Fig. 4(a).[32] The thermal stability of organic electrolytes containing both salts and solvents is at

the middle state between those of salts and solvents alone. In a real situation where the electrolyte, electrode (sodiated state) or SEI co-exist, the resulted metastable state may further narrow the thermal stability window.[26,31,33] Some effective additives like fluoroethylene carbonate (FEC)[26] or ethoxy(pentafluoro)cyclotriphosphazene (EFPN)[34] were reported to benefit the thermal stability and even reduce the inflammability of carbonate electrolyte via building stable SEI films. Furthermore, the ionic liquid-based electrolyte with low volatility and flammability can significantly improve the safety of NIBs.[35] For example, Wu *et al.* demonstrated a novel $NaPF_6$ in 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide (BMITFSI) electrolyte for $Na_3V_2(PO_4)_3$ and its decomposition temperature (> 350 ℃) (Fig. 4(b)) is higher than most of typical carbonate electrolytes (100–200 °C) as shown in Fig. 4(b).[36] However, the major concern is the high cost of ionic liquid and uncertain effective SEI formation.[37,38] Recently, Wang *et al.* developed a superconcentrated phosphate-based electrolyte (3.3 M $NaN(SO_2F)_2$ (NaFSI) in trimethyl phosphate (TMP)) as the fire-extinguishing component for safe NIBs, as shown in Fig. 4(c).[39] This salty solution enables hard carbon with robust inorganic SEI coverage to facilitate the stable cycling. Actually, salt-concentrated battery electrolytes have intrinsic thermodynamic stability with the suppressed side reactions and wide operating temperature/voltage window due to unique anion-derived functional SEI.[40] Besides improving the salt concentration, increasing the fluorine ratio in electrolyte is another effective way to improve safety of NIBs considering the robust NaF composition. Jiang *et al.* used tris(2,2,2-trifluoroethyl) phosphate (TFEP) with 0.9 M NaFSI to achieve both compatibility for carbon anode and thermal stability, as shown in Figs. 4(d) and 4(e).[41] Some inorganic components such as nitrogen, sulfur, fluorine, and phosphorus-containing compounds often deliver effective dynamics protection for electrodes and cause flame-retarding effect. Moreover, some ether solvents were reported to have low flammability,[42,43] which are very promising as the ether-based electrolyte tends to form compact and thin SEI in NIBs.[22,44]

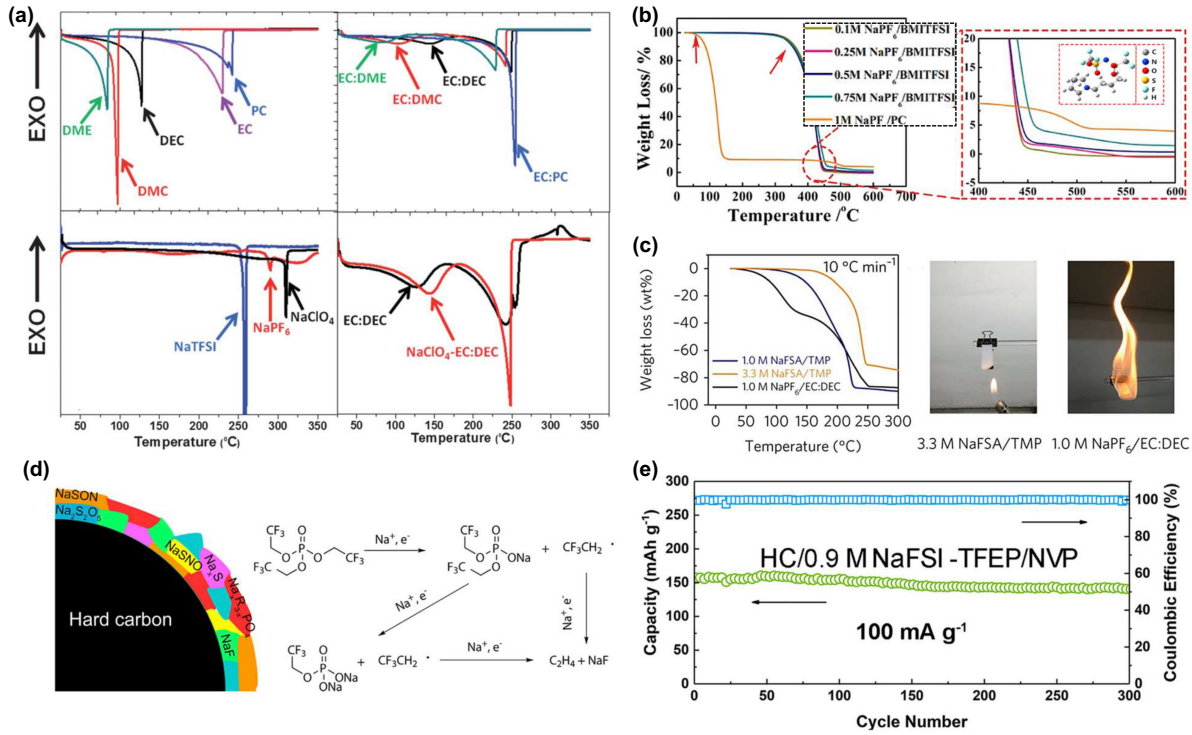


Fig. 4. (a) DSC heating curves up to 350 °C of solvents alone, solvent mixtures,propylene carbonate (PC) based electrolytes with 1 M of various Na salts, and ethylene carbonate (EC): diethyl carbonate (DEC) solvent mixture with or without a sodium salt (1 M $NaClO_4$).[32] (b) TG curves of the $NaPF_6$/PC electrolyte and the $NaPF_6$/BMITFSI electrolytes range from room temperature to 600 °C.[36] (inset: the chemical structures of the cation and anion components of BMITFSI) (c) Left: Weight loss of laboratory-made NaFSA (NaFSI) /TMP electrolytes and conventional 1.0 M $NaPF_6$/EC:DEC (1 : 1 vol.%) electrolyte in the thermogravimetric test. Right: flame tests of laboratory-made 3.3 M NaFSA/TMP electrolyte and conventional 1.0 M $NaPF_6$/EC:DEC (1 : 1 vol.%) electrolyte.[39] (d) Schematic illustration of the SEI layer and possible mechanism for the decomposition of the TFEP-derived interlayer. (e) Cycling performance at 100 mA/g of the hard carbon/$Na_3V_2(PO_4)_3$ full cell.[41]

In general, there is still a significant risk of flammability in organic liquid electrolyte which stimulates more development of new electrolyte systems including mainly aqueous and solid analogues, and both of them have their own characteristics. The aqueous system directly uses water as solvent with intrinsic safety and environmental friendliness but suffers a narrow electrochemical stability window (1.23 V).[45] Suo *et al.* improved the ratio of salt to water (so called

"water in salt") to enhance the operating window of NIBs (2.5 V) and the dynamics of electrode reaction is still superior with such high salt concentration, as shown in Figs. 5(a) and 5(b).[46] Obviously, aqueous NIBs are not suitable for high temperature working environment, but a solid state electrolyte usually performs better in a higher operating temperature due to the smaller barriers of Na^+ transport.[47,48] $Na_3Zr_2Si_2PO_{12}$ with 3D NASICON framework can deliver an ionic conductivity of 1.5×10^{-3} S/cm at 200 °C.[49] Only a tiny reversible thermal reaction at 155 °C was found during the heating process and this reversible thermal behavior was also found in $Na_3V_2(PO_4)_3$ with similar NASICON structure (related to structure transitions), as shown in Fig. 5(c). The final all solid state NIB based on $Na_3Zr_2Si_2PO_{12}$ electrolyte and $Na_3V_2(PO_4)_3$ symmetric electrodes can work at 200 °C with good reversible capacity. But inorganic oxide electrolytes with terrible interfacial contact usually weaken the capacity retention.[47] It is necessary to introduce some flexible components to achieve both safety and interfacial compatibility. For example, Kim *et al.* designed a novel hybrid solid electrolyte mixing with $Na_3Zr_2Si_2PO_{12}$, poly(vinylidene fluoride–hexafluoropropylene) (PVdF-HFP), and 1 M sodium triflate ($NaCF_3SO_3$) in tetraglyme (TEGDME) liquid electrolyte.[50] This combination enabled a flexible NIB and improved the thermal decomposition temperature (Fig. 5(d)). A further shrinkage comparison test at 120 °C indicated a good thermal stability compared with the commercial membrane (Celgard), as shown in Fig. 5(e). Based on this hybrid electrolyte film, a flexible solid NIB with hard carbon anode and $NaFePO_4$ cathode can run 200 cycles without obvious capacity loss due to the synergistic effect of the ceramic fillers and polymer skeleton. Recently, Liu *et al.* *in situ* built a robust AlF_3 coating layer taking advantage of the reaction between Al_2O_3 and the NaFSI hydrolysis products, which improved the interfacial stability of PEO-based NIBs.[51] The introduction of Al_2O_3 nanoparticles can enhance the thermal stability (Fig. 5(f)) and the remove of residual water can reduce side reactions (Fig. 5(g)). In addition, the emerging *in situ* polymerization technology is also a convenient method to achieve safe NIBs as an upgradation of the tradition organic liquid electrolyte[52] and it needs to reduce extra initiators and obtain controlled polymerization in the future.[53]

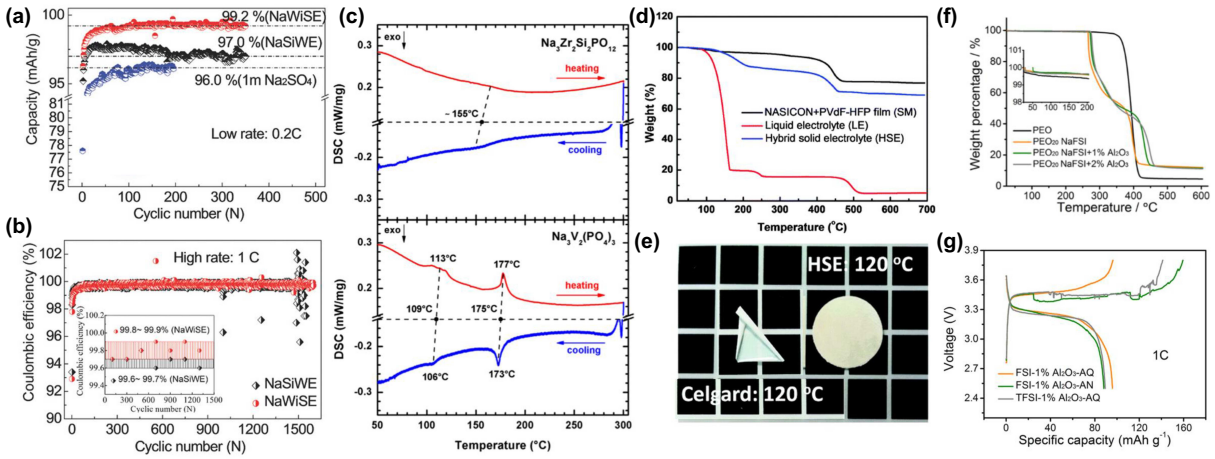


Fig. 5. (a), (b) Electrochemical performances of $Na_{0.66}[Mn_{0.66}Ti_{0.34}]O_2/NaTi_2(PO_4)_3$ full cell in different aqueous electrolytes (NaSiWE: 2 M $NaCF_3SO_3$, NaWiSE: 9.26 M $NaCF_3SO_3$, and 1 M Na_2SO_4). (a) Coulombic efficiency at low rate. (b) Cycle life at high rate.[46] (c) DSC data, recorded under Ar at 10 °C/min, of $Na_3Zr_2Si_2PO_{12}$ (top) and $Na_3V_2(PO4)_3$ (down).[49] (d) TGA results for the composite solid film, ether-based liquid electrolyte (1 M $NaCF_3SO_3$/TEGDME), and NASICON-based composite hybrid solid electrolyte (HSE). (e) Shrinkage of commercial membrane (Celgard) and HSE at 120 °C.[50] (f), (g) Characterization of the neat PEO and as-prepared PEO_{20}NaFSI $+x$ wt.% Al_2O_3 ($x = 0$, 1, 2) blended polymer electrolyte: (f) TGA traces from 30 °C to 600 °C (the inset is an enlarged image from 30 °C to 200 °C); (g) typical charge and discharge curves of $Na_3V_2(PO_4)_3$ half-cells at the 1 C rate at 80 °C. (AQ: aqueous process; AN: acetonitrile as solvent).[51]

5. Conclusion and outlook

With the industrialization of NIBs, the safety issues (especially, thermal stability) and related failure analysis are critical for their large-scale energy storage applications.[54] As summarized in Fig. 6(a), different material systems obviously have different thermal behaviors. The actual safety of a complete battery system depends more on the anode and electrolyte side, and an optimal combination of various electrolytes and electrodes towards safe NIBs is compelling.

In the short term, NIBs with carbon anode and oxide cathode with organic liquid electrolyte have promising application prospect considering their cost and performance. Some recent reports have already demonstrated a high safety in pouch cells based on the above material system,[10] while the special safety mechanisms should be further clarified (high stable Al current collector and disordered carbon anode may be the key compared with the Cu current collector and graphite anode in Li-based system). Building stable SEI and CEI can further enhance the thermal stability. High safety phosphates, solid state

electrolytes, salt-concentrated electrolytes, etc. are worth investigation in the future. Besides electrolytes and electrodes, the selection of separators, current collectors, and other components also has a deep influence on the safety of NIBs and the introduction of some smart materials including overcharge protection additives,[55] thermal responding reagents, etc. inspired from the design strategy of safe LIBs is necessary.[56]

In addition, accurate characterization methods need to be further developed to capture the detailed thermal parameters of NIBs. Very recently, we used a new constant-volume-type DSC (creating confined space to simulate closed battery environment) to make a comparison between the standard Li- and Na-based electrolytes. It is found that the Na-based system exhibits a better thermal stability than its Li counterpart from the less total heat generation or higher temperature of the exothermic peak of the Na-based system in Fig. 6(b), which suggests a safety advantage of NIBs and will be further reported in another paper. Note that the accumulated data about the safety or failure modes of NIBs have not reached the standard requirements of industrialization including the consideration about different operating conditions (100% state of charge and abuse tests, especially) and different structural types of NIBs (some high-capacity cells such as pouch cells, cylinder cells, prismatic cells, etc., especially), which needs a systematic research (like LIBs). The safety study about the battery pack is also important because of the application potential of NIBs in grid storage. Meanwhile, it should be considered to establish a more reliable safety database of NIBs to help identify the specific failure mechanism via multiscale characterizations with some *in situ* self-monitoring devices.

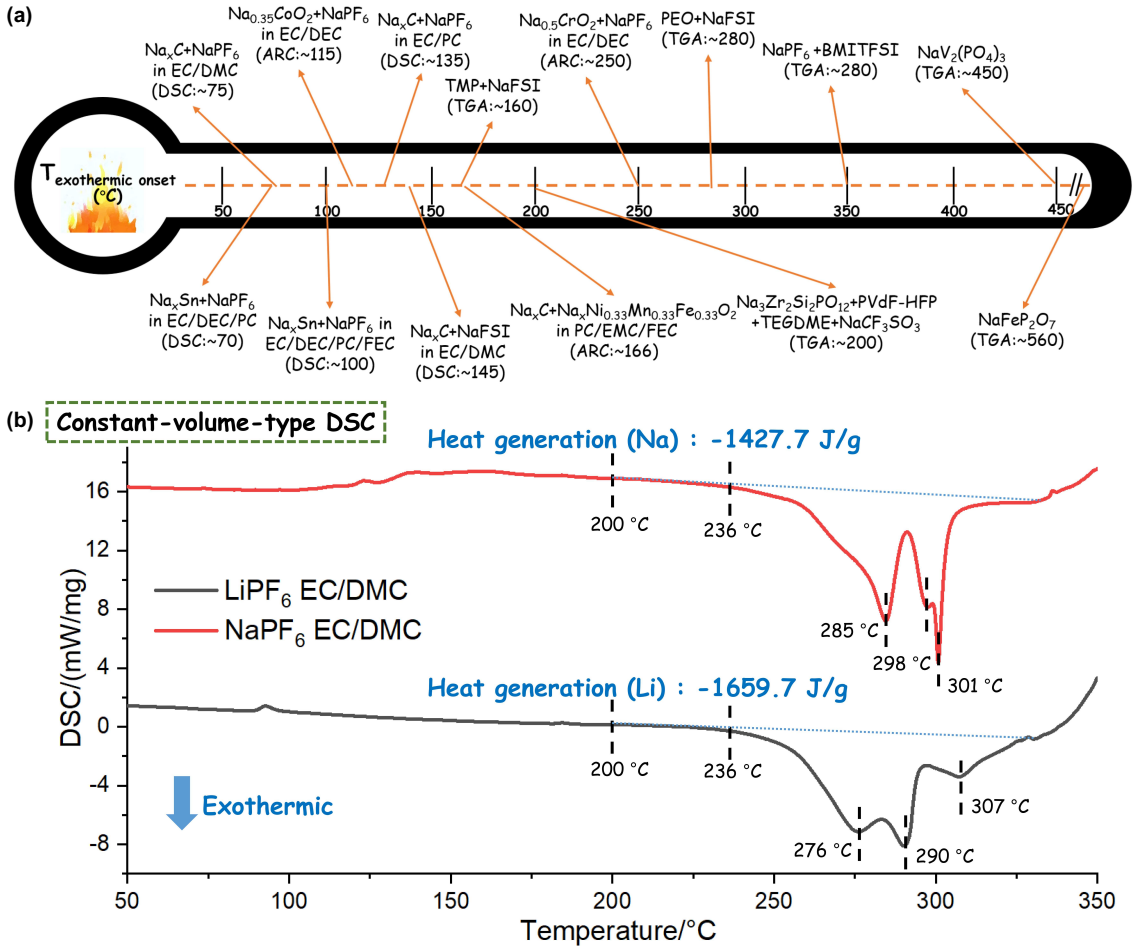


Fig. 6. (a) A summary of the exothermic onset temperatures about the different electrolytes and electrodes of NIBs which are related to thermal stability.[11,12,14,26,31,33,36,39,50,57] (b) Constant-volume-type DSC (using sealed gold-plated crucibles) profiles of 1 M $NaPF_6$ in EC/DMC (1 : 1 vol.%) vs. 1 M $LiPF_6$ in EC/DMC (1 : 1 vol.%).

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