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Article type: Research News**Thermal-responsive Polymers for Enhancing Safety of Electrochemical Storage Devices***Hui Yang, Wan Ru Leow and Xiaodong Chen**

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Abstract: Thermal runaway constitutes the most pressing safety issue in lithium-ion batteries and supercapacitors of large-scale and high-power density due to risks of fire or explosion. However, traditional strategies for averting thermal runaway do not enable the charging-discharging rate to change according to temperature, or the original performance to resume when the device is cooled to room temperature. To efficiently control thermal runaway, thermal-responsive polymers provide a feasible and reversible strategy due to their ability to sense and subsequently act according to a pre-determined sequence when triggered by heat. Herein, we reviewed the recent research progress on the use of thermal-responsive polymers to enhance the thermal safety of electrochemical storage devices. First, a brief discussion was provided on the methods of preventing thermal runaway in electrochemical storage devices. Subsequently, a short review was provided on the different types of thermal-responsive polymers that can efficiently avoid thermal runaway, such as phase change polymers, polymers with sol-gel transitions, and polymers with positive temperature coefficient. The results represent the important development of thermal-responsive polymers towards the prevention of thermal runaway in next-generation smart electrochemical storage devices.

1. Introduction

With the rapid development of consumer electronics such as phones, laptops and electric cars, the past two decades have witnessed a great surge in interest towards electrochemical storage devices with high energy densities, ultrafast charging rates, and long cycle lives.^[1-6] However, the energy transfer process still poses serious safety issues, especially in lithium-ion batteries and supercapacitors of large-scale and high-power densities.^[7-10] The most important of these safety issues would be thermal runaway, as it gives rise to great dangers such as fire or explosion, which would threaten the health and safety of electronics consumers.^[11-19] Thermal runaway occurs when a large amount of heat is generated as a result of high power supplied by rapid current flow.^[20-21] If the heat is unable to quickly dissipate, it would lead to temperature increase.^[22-23] With the continuous looping of this uncontrolled positive feedback, the device would rapidly reach an extremely high temperature, which may lead to fire or explosion.^[24-29] From this, it can be seen that the effective control of thermal runaway in electrochemical storage devices constitutes an important issue for investigation.

To effectively control thermal runaway, two strategies have been developed. The first strategy is the use of physical safety designs to release high pressure and heat accumulated in the devices prior to thermal runaway, such as the incorporation of safety vents, thermal fuses, shutdown separators, and special management systems.^[30-32] However, these physical safety designs, i.e., thermal fuses as disposable solutions for thermal runaway, merely lower the risks of fire or explosion, and may result in an increase in the magnitude of the danger.^[33-34] For example, safety vents, which release the gas accumulating inside the devices due to rising pressure and temperature, are not entirely fire or explosion proof; the outside air may subsequently enter the devices and react with the active electrolyte or electrode, resulting in ignition and explosion.^[35] The second strategy is the fabrication of inherently safe device materials, such as temperature-sensitive electrode materials, solid-state electrolytes with low

conductivity, electrolytes with lower flammability, as well as additives that protect from overcharging. Compared to the first strategy, this method endows energy storage devices with active protection behavior and much higher safety working temperatures.^[36-41] However, this strategy is not entirely foolproof as the thermal stability and compatibility of these materials are yet not well-studied. Therefore, the development of a novel, smart, and reversible strategy to solve thermal runaway remains one of the challenges and opportunities for the next-generation smart electrochemical storage devices.^[42]

Thermal-responsive polymers, which are capable of reversible phase changes, sol-gel transitions, or are characterized by positive temperature coefficients, are expected to be a viable strategy for preventing thermal runaway towards the fabrication of safer electrochemical storage devices. This is achieved by efficiently inhibiting the ionic or electron conduction between electrodes through molecular conformation changes of the polymers, which can efficiently control the activity of conductive materials in the devices. **(Figure 1)**.^[43-49] Specifically, the electrochemical storage devices are able to function well at room temperature due to free migration of ions or electrons between the electrodes. During thermal runaway, the molecular conformation changes of the polymers are triggered by temperature increase, leading to significant changes in functional properties such as hydrophilic-hydrophobic property, electrical conductivity, and mechanical properties. These changes result in the efficient inhibition of ionic or electron conduction between the electrodes, which prevents temperature increase and in turn fire and explosion. An example is the use of a thermal-responsive copolymer comprising acrylic acid and *N*-isopropylacrylamide (NIPAM) to control ionic conductivity via phase transition from the hydrophilic to hydrophobic state.^[46-48] When the solution temperature exceeds the lower-critical solution temperature (LCST) of the copolymers, the copolymers would precipitate and reduce the amount of conductive ions between electrodes.^[49-50] Similar thermal-responsive

polymers P(NIPAM-co-SPMA) and PMABS (**Table 1**) can also be coated onto the substrate as ion channels to control the migration of ions between electrodes at high temperature.^[51-53]

In this research news, we summarized the recent progress in the application of reversibly thermal-responsive polymers towards the efficient control of thermal runaway in electrochemical storage devices. We also discussed possible strategies and future designs of safer electrochemical storage devices that avoid thermal runaway via reversibly thermal-responsive polymers. We believe that the utilization of reversibly thermal-responsive polymers for safer electrochemical storage devices could create great opportunities for next-generation smart electrochemical storage devices, which are free from the threat of thermal runaway.

2. Reversible phase transition

The reversible phase transition process of thermal-responsive polymers is used for efficiently inhibiting thermal runaway. At room temperature, thermal-responsive polymers can be uniformly dispersed in the solvent and rendered relatively free to move.^[54-55] When the temperature increases, the phase transition of the polymers causes them to physical cross-link in the solvent to form a three-dimensional network.^[56-60] This would result in great changes in the interior microstructures of the polymers, such that free movement of polymer chains and their surrounding conductive molecules would be inhibited.

An example of the aforementioned thermal-responsive polymers is PNIPAM, which dissolve in aqueous solutions below 32-34 °C but undergo phase separation from the hydrophilic state to the hydrophobic state at high temperatures due to disruption of the hydrogen bonds between the *N*-isopropyl groups and water.^[61-72] The unique phase transition of PNIPAM was employed to enable the self-protection of electrochemical storage devices from overheating (**Figure 2a**).^[49] At low temperatures, PNIPAM/acrylamide (AM) is soluble in the electrolyte solution and the conductive Li ions are able to move freely. When the

temperature exceeds the LCST, the electrolyte solution containing PNIPAM/AM would undergo a phase transition of PNIPAM from the hydrophilic to the hydrophobic state, leading to the formation of hydrogels. The formation of hydrogels was demonstrated to inhibit the migration of conductive ions and eliminate the conductive pathway between the electrodes (Figure 2b). The experimental data showed that the D_{Li} of the thermal-responsive supercapacitor was reduced from 1.9×10^{-13} to $7.6 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ upon heating from 20 to 70 °C, which led to the decrease in C_{spe} from 52.5 to 34.0 F g⁻¹ (Figure 2c). The reduction in conductivity of the thermal-responsive supercapacitor based on temperature increase was visually demonstrated through incorporation into a simple circuit containing an LED light. Upon increasing the temperature to 60 °C, the light intensity of LED decreased from 1.39 to 0.41 mW (Figure 2d), which was indicative of the smart thermal self-protection capability of the supercapacitor. Thus, the use of reversible phase transition of thermal-responsive polymers to inhibit the migration of ions at high temperatures is a viable strategy to efficiently prevent thermal runaway in electrochemical storage devices. We believe that such strategy can be widely applied in the fields of intelligent electrochemical storage devices and smart materials in order to facilitate optimal performance within a defined temperature window.^[73]

The phase transition from solid to liquid can also be applied to the fabrication of shut-down separators for enhancing the safety of various batteries.^[74-77] In a recent work, triphenyl phosphate (TPP), an organophosphorus-based flame retardant, was encapsulated within poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) to fabricate a core-shell microfiber separator (TPP@PVDF-HFP) with thermal-triggered flame-retardant properties for lithium-ion batteries.^[76] When the battery was running as per normal, TPP@PVDF-HFP did not influence the performance of battery due to its insolubility in the electrolytes. During the occurrence of thermal runaway, however, the PVDF-HFP polymer shell underwent phase transition from solid to liquid as the temperature increased to that of the PVDF-HFP melting point (~160°C), which is lower than the temperature of combustion. The encapsulated TPP

was then released into the electrolyte, thus effectively inhibiting the combustion of flammable electrolytes. Similarly, poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) were employed to fabricate core-shell separators PLA@PBS for full cells assembled with LiFePO₄ cathodes and graphite anodes.^[77] The thermal-responsive separator not only exhibited high electrolyte affinity and ionic conductivity, but also possessed the propensity for thermal shut-down when the temperature was increased to that of the melting point (130 °C). Although the melting processes of PVDF-HFP and PLA@PBS can only be used to inhibit the combustion of flammable electrolytes for a single time, we believe that this class of smart separators based on phase transition will be highly useful in solving the thermal runaway safety issues of other large-format cells in the future.

3. Reversible sol-gel transition

The reversible sol-gel transition of polymers is also another process that can be used for the thermal protection of electrochemical storage devices. In the solution state, conductive ions are relatively free to move in the polymer solution. When the temperature increases, sol-gel transition would occur through cross-linking of the polymer chains, which would inhibit free movement of the conductive ions in the gel system. This enables the efficiently control of the thermal runaway of electrochemical storage devices. An example of such polymers is pluronic poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-PPO-PEO), which was used as electrolyte to control the migration of H⁺ or Li⁺ as conductive ions between electrodes (**Figure 3a**).^[50] At low temperatures, the electrolyte was in the solution state due to the hydrophilicity of PEO and the micellar structure formed by the hydrophobic polymer segments PPO, which enabled H⁺ or Li⁺ ions to move freely between electrodes. When the temperature was increased, the merging of closely packed micelles formed by PPO and the entanglement of the PEO segments resulted in the first sol-gel transition. With further increment in temperature, the PEO-PPO-PEO concentration would

exceed the critical concentration and lead to a second sol-gel transition.^[78-80] These sol-gel transitions of the electrolyte inhibited the free migration of ions between electrodes, resulting in the shut-down of the current (Figure 3b). The degree of capacity loss at high temperatures was also increased from 50% to nearly 100%. Based on this thermal-responsive property of the PEO-PPO-PEO electrolyte, a supercapacitor with thermal protection capability was fabricated. Upon heating the supercapacitor to 70 °C, the light intensity of the connected LED was significantly reduced (Figure 3c).

The aforementioned studies demonstrated that the novel strategy of utilizing sol-gel transition, a rapid and reversible process triggered by temperature, can be efficiently used to control the thermal runaway of electrochemical storage devices. We believe that various thermal-responsive polymers with the capability for sol-gel transition can also be used to prevent thermal runaway in electrochemical storage devices. To satisfy the thermal protection requirements of electrochemical storage devices in various environments, the temperature of the sol-gel transition can be easily adjusted through mere selection of compatible thermal-responsive polymers.

4. Positive temperature coefficient (PTC)

Reliable and high-performance lithium-ion batteries (LIBs) are garnering great interest due to their ability to supply large amounts power to electronic devices.^[81] The thermal runaway of LIBs with high densities and ultrafast charging rates remains an important and unresolved issue.^[8] Commercial LIBs tend to be equipped with external safety vents and PTC resistors for preventing thermal runaway. However, the pressure and temperature generated by thermal runaway inside LIBs increase too fast for detection by these external devices.^[82] In addition, the application of PTC resistors is limited by low conductivity and considerable leakage current at room temperature.^[83] Therefore, the use of thermal-responsive polymers

for smart electrodes will provide an opportunity and challenge for solving thermal runaway of LIBs.

To address the problem of thermal runaway in LIBs, fast and reversible thermal-responsive electrodes with PTC were fabricated by the internal incorporation of electrode and thermal-responsive materials (**Figure 4a**).^[51] These thermal-responsive materials were composed of conductive graphene-coated spiky nanostructured nickel particles as the conductive filler, as well as polyethylene (PE) with a large thermal expansion coefficient as the matrix, which endows them with excellent PTC. The graphene coated on the surface of nickel particles provided high electrochemical stability towards oxidation and electrolyte decomposition in LIBs. Due to the nano-spikes on the particle surface, the thermal-responsive materials displayed a high electrical conductivity of 50 S cm^{-1} at room temperature, which was about 100 times higher than that of common conductive polymer composites. Upon increasing the temperature, the expansion of PE volume increased the distance between the nickel particles, leading to a reduction in the electrical conductivity. The electrode conductivity decreased by seven to eight orders of magnitude in less than 1 s when the temperature was increased to 80°C (**Figure 4b**), which enabled thermal protection in the LIBs during thermal runaway. Correspondingly, the resistance of the thermal-responsive materials increased from 2 to $10^8 \Omega$ in less than 1 s. These smart LIBs with thermal protection also demonstrated both excellent cell function in a wide voltage window at normal temperatures, and fast shut-down under abnormal conditions (**Figure 4d**).

Although thermal polymers with PTC have been successfully applied towards the prevention of thermal runaway in LIBs, its feasibility remains limited by the size of LIBs and the maximum temperature during thermal runaway. It should be also noted that when the size and thickness of LIBs are increased, the internal heat caused by thermal runaway will be quickly delivered between electrodes and further promote the reaction in the LIBs. Within a short time, the temperature of the LIBs may reach the melting point of polymers in the

substrate, which leads to the failure of the shut-down function of these smart thermal-responsive electrodes. To develop more effective thermal-responsive materials for the safety management of large consumer batteries, next-generation thermal-responsive polymers with PTC will be designed towards high melting point and ultrafast sensitivity towards temperature.

5. Conclusion and Outlook

A wide variety of thermal-responsive polymers (Table 1) with phase change, sol-gel transition, and PTC properties have already been employed to avoid the thermal runaway of electrochemical storage devices through efficiently controlling the free migration of conductive ions and electrons between electrodes with increasing temperature. However, current thermal-responsive polymers with phase change and sol-gel transition properties are only able to realize thermal self-protection in supercapacitors, while thermal-responsive polymers with excellent PTC are limited by the size of the battery. Moreover, the addition of these thermal-responsive polymers into the electrochemical storage devices for preventing thermal runaway would reduce the energy density as these polymers increase the weight of the whole devices but do not contribute to the generation of energy. Therefore, there remains a long way to go before thermal-responsive polymers can be applied towards the prevention of thermal runaway in electrochemical storage devices.

In the future, multifunctional polymers can be designed and fabricated to solve the thermal runaway. These polymers would first fulfil the base requirements of generating thermal responses when the temperature is higher than the working temperature of devices. In addition, the polymers can serve as commercial binders in the energy devices for binding active materials on the metal electrodes or separators used to limit charge migrations to that of ions. Thus, multifunctional polymers would be able to efficiently control the thermal runaway without increasing the weight of the devices. Based on these discussions, we can foresee that thermal-responsive polymers that are also able to function as binders and

separators will be rapidly developed towards enhancing the safety of electrochemical storage devices.

With the rapid development of wearable devices, flexible high-performance electrochemical storage devices such as LIBs are garnering great interests as they not only supply power to devices such as electronics, software, and sensors, but also have the potential to be worn on the body as implant or accessories.^[84-86] The issue of safety for such devices is very important because they undergo bending and stretching when used on the body. If these devices generate fire or explosions when worn on the body, they will cause unimaginably serious consequences for the human wearers. For example, wearable solar cells are attracting more and more attention due to their potential for harvesting green energy, low pollution, and longtime-use with no need of charging. However, there remains a big problem of unstable charging and over-charging in LIBs through the solar cells, as solar cells convert sunlight of different light densities to generate electricity for LIBs. To address this issue, flexible photo-responsive polymers and three-dimensional (3D) printing technology may be used to fabricate various photo-responsive solar cells with high safety.^[87]

In addition, the thermal runaway of flexible LIBs with high density and ultrafast charging rate remains an important yet unresolved issue; the risks of fire or explosion are increased when the LIBs are subjected to mechanical abuse. To solve this problem, thermal-responsive functional polymers should be endowed with flexibility to prevent thermal runaway in flexible LIBs. This would enable smart electrodes and electrolytes based on the flexible thermal-responsive polymers to be bended and stretched according to the shape change of flexible LIBs. For example, stretchable gels with phase transition properties can be employed as smart electrolytes to prevent the thermal runaway of flexible LIBs. At room temperature, conductive active ions and electrons between electrodes can move freely within the stretchable gels. During thermal runaway, the phase transition occurs, in which the gels undergo further cross-linking to stop the free migration of conductive active ions and

electrons. Moreover, flexible thermal-responsive polymers with excellent PTC can also be used to prevent thermal runaway of flexible LIBs. With the increase in temperature caused by thermal runaway, the resistance of thermal-responsive materials would increase, leading to the shut-down of current inside flexible LIBs. We believe that thermal-responsive polymers with various functions will bring great challenges and opportunities for solving the thermal runaway issue in next-generation electrochemical storage devices with high-performance, which can be used in different places from human body to deep space.

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Figure 1. Illustration of the migration inhibition of the ionic or electron conduction between electrodes via reversibly thermal-responsive polymers for preventing the thermal runaway of electrochemical storage devices.

Figure 2. a) The structure of thermal-responsive polymers based on NIPAM and AM. b) Illustration of sol-gel transition of electrolyte that inhibits the ions migration between the electrodes. c) The specific capacitances of supercapacitors with PNIPAM/AM decrease with increasing temperature. d) Demonstration of supercapacitor' self-protection through sol-gel transition.^[49] Copyright 2015, Wiley-VCH.

Thermal-responsive polymer PEO-PPO-PEO

Figure 3. a) The structure of thermal-responsive polymers PEO-PPO-PEO. b) Illustration of thermal-responsive sol-gel system for electrochemical storage devices. c) Demonstration of self-protection of the supercapacitor by sol-gel transition of electrolyte.^[50] Copyright 2016, Wiley-VCH

Figure 4. a) The structure of polymer substrate PE and thermal switching mechanism of the thermal-responsive materials PE/GrNi. At room temperature, the ON state of LED light indicated the work well of the battery due to the quantum tunneling effect enabled by the spiky nanostructure (GrNi). With heating caused by thermal runaway, the TRPS was activated and greatly increased its resistance, which could shut down the battery and LED light (OFF state). Upon cooling, the polymer recovered to the original conductive pathways, leading to the ON state of LED light. b) Resistivity of different thermal-responsive films increases with increasing temperature. c) Resistance change of PE-based composites with different conductive fillers on heating. d) Demonstration of thermal switching behavior of the thermal-responsive film based on PE and GrNi.^[51] Copyright 2016, Nature Publishing Group.

Table 1. Various thermal-responsive polymers for avoiding thermal runaway of electrochemical storage devices

Thermal-responsive polymers	Structure	Roles in electrochemical storage devices
PNIPAM/AA ^[46]		Electrolyte
PNIPAM/AM ^[49]		Electrolyte
PEO-PPO-PEO ^[50]		Electrolyte
PE ^[51]		Electrode
P(NIPAM-co-SPMA) ^[52]		Electrode
PMABS ^[53]		Electrolyte
PVDF-HFP ^[76]		Separator
PBS ^[77]		Separator

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Thermal-responsive polymers provide a feasible and reversible strategy to efficiently control thermal runaway due to their ability to sense and subsequently act according to a pre-determined sequence when triggered by heat. A short review was provided on using thermal-responsive polymers to efficiently avoid thermal runaway, such as polymers with phase changes, polymers with sol-gel transitions, and polymers with positive temperature coefficient.

Keywords: thermal runaway, electrochemical storage devices, thermal-responsive polymers

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Thermal-responsive Polymers for Enhancing Safety of Electrochemical Storage Devices