

Low-volatile binder enables thermal shock-resistant thin-film cathodes for thermal batteries

Yong Xie¹, Liang Dong¹, Xu Zhang¹, Yong Cao¹, Yan Cui¹, Xiao Liu¹, Yi Cui¹, Chao Wang¹, Hongfa Xiang², Xuyong Feng², and Long Qie³

¹China Academy of Engineering Physics Institute of Electronic Engineering

²Hefei University of Technology

³Huazhong University of Science and Technology School of Material Science and Engineering

July 27, 2023

Abstract

Manufacturing thin-film components is crucial for achieving high-efficiency and high-power thermal batteries (TBs). However, developing binders with low gas production at the operating temperature range of TBs (400-550 °C) has proven to be a significant challenge. Here we report the use of acrylic acid derivative terpolymer (LA136D) as a low-volatile binder for thin-film cathode fabrication and studied the chain scission and chemical bond-breaking mechanisms in pyrolysis. It is shown LA136D defers to random-chain scission and cross-linking chain scission mechanisms, which gifts it with a low proportion of volatile products (ψ , $\psi=39.2\text{wt}\%$) at even up to 550 °C, well below those of the conventional PVDF (77.6wt%) and SBR (99.2wt%) binders. Surprisingly, LA136D contributes to constructing a thermal shock-resistant cathode due to the step-by-step bond-breaking process. This is beneficial for the overall performance of TBs. In a 130 s pulse discharging test, the thin-film cathodes exhibited a remarkable 440% reduction in polarization and 300% enhancement in the utilization efficiency of cathode materials, while with just a slight increase of 0.05 MPa in gas pressure compared with traditional “thick-film” cathode. Our work highlights the potential of LA136D as a low-volatile binder for thin-film cathodes and shows the feasibility of manufacturing high-efficiency and high-power TBs through polymer molecule engineering.

Article category: Full Paper

Subcategory: thermal battery, primary battery, reserve battery

Low-volatile binder enables thermal shock-resistant thin-film cathodes for thermal batteries

Yong Xie*, Xu Zhang, Liangping Dong, Yong Cao, Xiaojian Liu, Yixiu Cui, Chao Wang*, Yanhua Cui*, Xuyong Feng, Hongfa Xiang, and Long Qie

Dr. Y. Xie, Dr. X. Zhang, Dr. L. P. Dong, Dr. Y. Cao¹, Prof. X. J. Liu, Prof. Y. X. Cui, Dr. C. Wang, Prof. Y. H. Cui

Laboratory of Electrochemical Power Sources, Institute of Electronic Engineering, China Academy of Engineering Physics, Mianyang, Sichuan 621000, China E-mail: yongxie@caep.cn (Y. Xie); wangchao-1988924@126.com (C. Wang); cuiyanhua@netease.com (Y. H. Cui)

Prof. X. Y. Feng, Prof. H. F. Xiang School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, Anhui, China

Prof. L. Qie

State Key Laboratory of Material Processing and Die & Mold Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

Keywords: thermal battery, thin-film cathode, low-volatile binder, gas production, high-power

Manufacturing thin-film components is crucial for achieving high-efficiency and high-power thermal batteries (TBs). However, developing binders with low gas production at the operating temperature range of TBs (400–550 °C) has proven to be a significant challenge. Here we report the use of acrylic acid derivative terpolymer (LA136D) as a low-volatile binder for thin-film cathode fabrication and studied the chain scission and chemical bond-breaking mechanisms in pyrolysis. It is shown LA136D defers to random-chain scission and cross-linking chain scission mechanisms, which gifts it with a low proportion of volatile products (ψ , $\psi=39.2\text{wt}\%$) at even up to 550 °C, well below those of the conventional PVDF (77.6wt%) and SBR (99.2wt%) binders. Surprisingly, LA136D contributes to constructing a thermal shock-resistant cathode due to the step-by-step bond-breaking process. This is beneficial for the overall performance of TBs. In a 130 s pulse discharging test, the thin-film cathodes exhibited a remarkable 440% reduction in polarization and 300% enhancement in the utilization efficiency of cathode materials, while with just a slight increase of 0.05 MPa in gas pressure compared with traditional “thick-film” cathode. Our work highlights the potential of LA136D as a low-volatile binder for thin-film cathodes and shows the feasibility of manufacturing high-efficiency and high-power TBs through polymer molecule engineering.

1. Introduction

High-temperature thermally activated reserve batteries (also known as thermal batteries or TBs) are primary (non-rechargeable), single-use reserve power sources characterized by long shelf-life (>20 years), high-power capability (pulse current reaches 1 A cm⁻²), and excellent environment adaptability (-60 to 90 degC), and widely used in modern weaponry and aerospace, such as missiles, artillery, ejector seats, and helicopter turbine.^[1-3] Next-generation of weaponry and aerospace equipment calls for TBs with higher power capability, reduced volume, and the ability to accommodate unconventional volume geometries, proposing an urgent need for innovative technologies of electrode preparation.^[4-6] The conventional manufacturing process for TBs, referred to as pressed-pellet, is limited to the production of thick (>250 μm) circular-shaped electrodes for it works directly by mechanical pressing rather than binder usage to form the electrodes.^[7,8] For most applications where the TBs’ working time is short, such as artillery fuze batteries and aircraft ejection seat batteries, the overall operation time does not exceed 100 seconds and the required thickness of electrochemically active materials does not exceed 100 μm .^[9] Electrodes produced using the pressed-pellet approach exhibit low utilization efficiency of active materials and possess excessive volume and weight compared to the mission requirements. Moreover, the thick electrodes increase the transport distance of ions and electrons, resulting in a high polarization and limited power capability of TBs. Furthermore, the restriction to circular-shaped electrodes hinders the shape-accommodation capability of TBs, which is especially crucial for space utilization in minimal environments.^[6,10-12]

Slurry-coating, which is extensively used in fabricating electrodes for commercial secondary lithium-ion batteries,^[13,14] is capable of continuously producing thin sheets with a thickness of 10–500 μm and shows great potential to break through pressed-pellet limitations.^[7,15,16] Nevertheless, one drawback of slurry-coating is the introduction of binders to the electrodes. These binders tend to thermally decompose and generate gases at the operating temperature of TBs (400 to 550 °C). This gas production within the hermetically sealed TBs can raise the internal gas pressure, posing serious risks such as deformation, cracking, or even explosion, which endanger surrounding electronics and explosive components. To prevent such catastrophic events, it is crucial to investigate the gas production resulting from binder decomposition and the ability of batteries to withstand increased gas pressure. However, current research primarily focuses on the adhesive strength of binders and their corresponding electrochemical performance, paying limited attention to gas production.^[17-19] Binders with low gas production at the operating temperature of TBs are the key to the success of slurry-coating. In real TBs stacks (including single-cells, pyrotechnic, ignition strips, insulation layers, battery case, and other functional components), once the maximum internal temperature is determined, the overall internal gas pressure (P) of TBs is decided by the initial gas content (P_o) and the gases produced by binder decomposition

(P_b). P_o depends on the total pore volume and gas species present in the battery stacks, typically falling within a constant range for typical TBs products. While on the other hand, P_b is closely associated with the proportion of gas released by the binder during thermal decomposition (which can be qualitatively described by the proportion of mass reduction (ψ)) and the binder content in the electrode (χ). The relationship governing P_b can be expressed as:

$$P_b = \frac{RT}{M} \frac{1}{V} \quad (1)$$

In equation (1), M signifies the average molecular weight of the gases, while R , T , and V represent the ideal gas constant, the internal temperature of TBs, and the volume of TBs respectively. Typically, pyrolysis of binders yields small molecules as gas products, and the value of M shows minimal variation across different binders. By equation (1), the key point in reducing P lies in the development of binders characterized by low ψ and low χ .

Previous works have studied the PVDF as a binder to fabricate thin-film cathodes for TBs.^[12,20] The PVDF-based cathodes have shown superior power capability compared to pressed-pellet cathodes and can be shaped into irregular forms. However, PVDF tends to produce volatile small molecules with high weight loss ($\psi = 77.6\text{wt}\%$ at 550°C) during thermal decomposition, which is not desirable for reducing the P of the TBs.^[21] Inorganic ceramic binders, such as glassy silicate (SiO_2/NaO),^[22] Poly(imide-co-siloxane) (PIS),^[17] and Na_2SiO_3 ,^[12] have attracted a lot of attention in recent years due to their higher thermal decomposition onset temperature (T_o , $450^\circ\text{C} < T_o < 550^\circ\text{C}$) and lower ψ compared to polymer binders. However, these ceramic binders are often having poor adhesion strength. Generally, the content of these electrochemically inactive and electronic-insulation ceramic binders in the electrodes (χ) reaches $5\text{wt}\%$ - $10\text{wt}\%$,^[12,22] significantly dilutes the electrodes' total capacity and power capability. To the best of our knowledge, there haven't been any reported binders that have both low ψ and do not compromise the electrochemical performance of thermal batteries (low χ). Moreover, previous studies on binders mainly focused on the performance of thermal battery single-cells, neglecting the investigation of performance in real hermetically sealed thermal battery stacks.^[19,20] Since gases released by the binder's thermal decomposition would dissipate in an open environment (the discharge tests of thermal battery single-cells are often conducted in an open environment), the negative impact on the internal gas pressure of thermal batteries cannot be detected in single-cell setups. Therefore, it would be more meaningful to study the binder's performance in real hermetically sealed thermal batteries to better understand its effects.

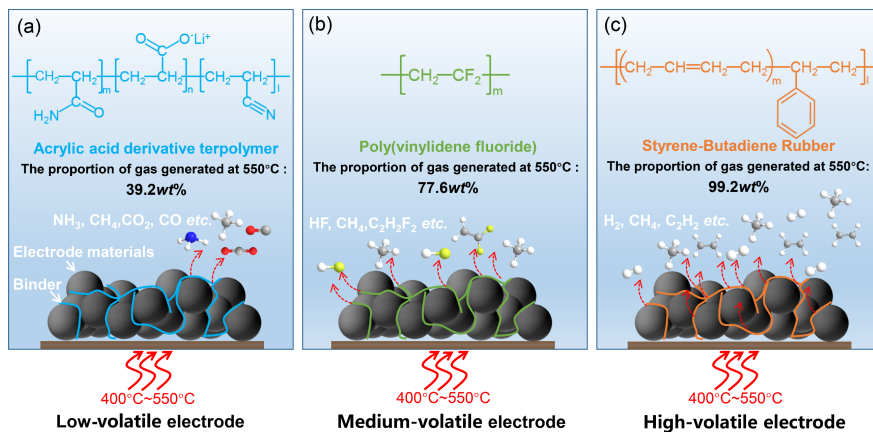


Figure 1. The gas production of electrodes with different binders. (a) Low-volatile electrode fabricated by acrylic acid derivative terpolymer binder (LA136D), the proportion of gases produced in acrylic acid derivative terpolymer thermal decomposition is only 39.2wt % at 550°C ; (b) Medium-volatile electrode fabricated by poly(vinylidene fluoride) binder, the proportion of gases produced in poly(vinylidene fluoride) thermal decomposition is 77.6wt % at 550°C ; (c) High-volatile electrode fabricated by styrene butadiene

rubber binder, the proportion of gases produced in styrene-butadiene rubber thermal decomposition is 99.2wt % at 550 °C.

According to polymer materials science,^[23,24] the ψ and χ values of organic polymers are tightly related to their molecule structure and molecular weight. Chemical bonds with high bonding energy are typically used to create thermal-resistant polymers. For example, -C[?]N (bond energy: 887 KJ mol⁻¹) and -CONH₂ (C=O, bond energy: 799 KJ mol⁻¹) are more stable at high temperatures compared to C-C (346 KJ mol⁻¹) and C-H (411 KJ mol⁻¹). Also, the ψ value of organic polymers is determined by the chain-scission mechanisms in pyrolysis. Polymers that undergo random-chain scission and cross-linking mechanisms in pyrolysis tend to have lower ψ values. On the other hand, polymers with end-chain scission mechanisms usually result in higher ψ values because they tend to involve the breaking off of a small unit or group at the end of the polymer chain, and generating a larger number of small volatile fragments. Among the commonly used polymers, poly(methyl acrylate) exhibits random-chain scission behavior and polyacrylonitrile follows cross-linking mechanisms. Both of these are desirable to construct low ψ binders for thin-film cathodes in TBs. The presence of highly polar groups like -C[?]N and C=O in polyacrylonitrile and poly(methyl acrylate) also contributes to achieving a strong adhesion strength by forming covalent bonds with the electrode materials. Which is beneficial to reduce the content of the binder in the electrodes (χ). In addition, polymers with higher molecular weight are also beneficial for enhancing thermal stability and bonding strength. Therefore, polyacrylonitrile or poly(methyl acrylate) multi-element polymer with a high molecule weight may be a good choice to fabricate thin-film cathodes of TBs.

In this work, we first studied the gas pressure durability of TBs with a typical size of Φ 83×83mm by using the COMSOL simulation platform and giving out a quantitative value that will deform TBs, which provides an instruction to develop binders with low gas production. Secondly, we reported acrylic acid derivative terpolymer (LA136D) with ultra-high molecule weight ($>100,000$) as a low-volatile binder to fabricate thin-film cathode for TBs (as shown in **Figure 1 (a)**), which shows both low gas-production and high adhesion capability. The performance of LA136D is verified in both thermal battery single-cells and stacks. Owing to the presence of polyacrylonitrile and poly (methyl acrylate), the ψ of LA136D is only 39.2wt % at even up to 550°C, well below the value of PVDF (77.6wt %) and SBR (99.2wt %), as shown in **Figure 1 (b)** and **(c)**. In our experiments, the content of LA136D in the electrode can be reduced to as low as 1wt % while maintaining excellent mechanical properties. Importantly, we found the rate of volatiles released in LA136D pyrolysis is step-by-step (slowly) due to the reasonable collocation of thermal stable (C[?]N, C=O) and hypo-thermal stable groups (C-C, C-H), this is truly beneficial to maintain the mechanical integrity of the cathode in the high thermal shock. Especially, in a 130s pulse discharging test, LA136D thin-film cathode stacks indicate a 77% reduction in polarization and 300% enhancement in cathode materials utilization efficiency, while with only ~0.05 MPa gas pressure increase compare with traditional pressed-pellet “thick-film” cathode.

2. Results and discussions

2.1. The gas pressure durability simulation of thermal battery

In this work, to reach the TBs stainless steel shell gas pressure durability value, a digital model of a thermal battery with 40xsingle cells is constructed in the COMSOL simulation platform. The detailed structure and parameters of the TBs model are shown in **Figure 2 (a)**. **Figure S1** and **Figure 2 (b)** show the simulation of the Von Mises Stress brought to a thermal battery stainless steel shell under different internal gas pressure. Generally, the highest temperature of the stainless-steel shell surface would not exceed 100degC even if the thermal battery’s internal temperature is high (the detail value is according to the thermal battery design requirement). The yield strength of stainless steel at 100 degC is about 230 MPa.^[25] From **Figure 2 (b)** we can see as long as the total internal gas pressure (P) in the thermal battery does not exceed 0.3 MPa, the Von Mises Stress brought to the stainless-steel shell would not exceed 220 MPa (even at the corners of column TBs, where are known to have severe stress concentration), and the stainless-steel would not go to experience any distortion. According to equation (1), the gases in TBs include two parts: the gases originally in the pores of TBs and produced by the thermal decomposition of materials in later periods. Commonly, the porosity of real TBs products is 30vol %~40vol %, herein, we assume the porosity of TBs to be 35vol %.

According to the size of the TBs model in this work, the P_o of original gases is calculated to be 0.149 MPa at 550 degC based on Ideal Gas Law ($PV=nRT$). Therefore, there is 0.151 MPa space for binder decomposition (P_b), as shown in **Figure 2 (c)**. That is to say, as long as the P_b is below 0.151 MPa, TBs would not be going to any distortion.

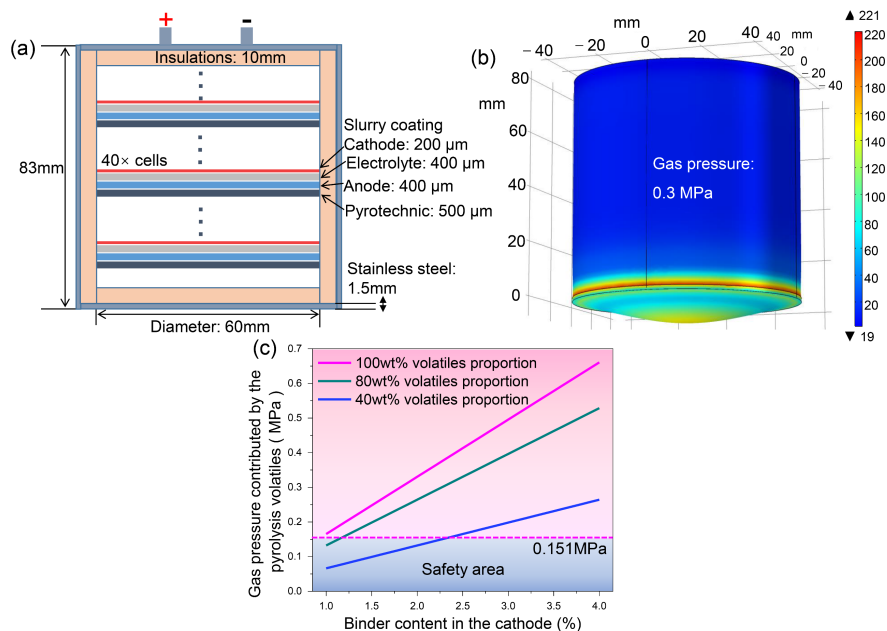


Figure 2. The simulation of gas pressure resistance of the thermal battery. (a) The schematics (2D) of the internal configuration of $\Phi 83 \times 83$ mm column thermal battery with 40 single-cells in the series; (b) the simulation of the Von Mises Stress (MPa) brings to the thermal battery stainless-steel shell under 0.3 MPa internal gas pressure, according to the simulation, the highest stress brings to stainless steel is about 220 MPa; (c) the relationships between thermal battery internal gas pressure (aroused by the thermal decomposition of binder), binder content in the cathode, and the proportion of volatiles generated in binder thermal decomposition at 550 °C.

Commonly, the volatile products in polymer binder pyrolysis are small molecules which with a similar average molecule weight. Here we presumably set an M of 25 according to the volatile products of PVDF and SBR binder in pyrolysis, as shown in Figure 1 (b) and (c).^[26,27] Combined with equation (1), we can reach the quantitative relationship between P_b , χ , and ψ , as shown in Figure 2 (c). From Figure 2 (c), to ensure the P_b lies in the security zones, the binders with high ψ should have low χ , *e.g.*, a binder with a ψ of 80wt % the χ in the cathode should not exceed 1.2wt %. In contrast, the binders with low ψ have a wider binder content space for choosing. *e.g.* binder with a ψ of 40wt % the binder content limit is 2.3wt %. From the simulation, we can get a guideline for selecting and designing binders for thin-film TBs.

2.2. The thermal properties of acrylic acid derivative terpolymer

Figure 3 (a) shows the TG curves of LA136D, PVDF, and SBR, the test is carried out in an N_2 atmosphere and the calefactive rate is $10^\circ C \text{ min}^{-1}$. From Figure 3 (a), all the binders show thermal decomposition. The thermal decomposition onset temperature (T_o) is about 260°C, 270°C, and 400°C respectively for SBR, LA136D, and PVDF. The lower T_o of SBR and LA136D are reasonable because of the presence of C-C and C-N bonds in the molecule structure which with an inferior bonding energy of 347 KJ mol^{-1} and 305 KJ mol^{-1} respectively. The higher T_o of PVDF is attributed to the high electronic negativity of fluorine atoms that affects the excursion of an electronic cloud of C-C and leads to the increase of thermal stability. In contrast to T_o , the ψ of the binders is more important in real hermetically sealed TBs. It directly relates to the P of

TBs. Figure 3 (a) shows LA136D having the lowest ψ of 39.2wt %, well below the value of PVDF (77.6wt %), and SBR (99.2wt %). The difference of ψ in the three binders can be interpreted by two aspects: 1) chain scission mechanisms, and 2) chemical bonding energy.^[28] According to polymer science, polyacrylonitrile and poly (methyl acrylate) parts defer to the cross-linking and random-chain scission mechanisms respectively in the pyrolysis, while PVDF and SBR defer to the random-chain scission mechanisms.^[23,24] Polymers with random-chain scission and cross-linking mechanisms often lead to a low ψ since the less small volatile fragments produced, while polymers with end-chain scission mechanism usually lead to high ψ due to it often involves the breaking of a small unit or group at the end of the chain, which results in many small volatiles fragments. Thus, the polyacrylonitrile and poly (methyl acrylate) parts in LA136D help it with a low ψ . On the other hand, chemical bonds with high energy are more stable at high temperatures. The double bonds (the bond energy of C=O is 799 KJ mol⁻¹) and triple bonds (the bond energy of C[?]N is 887 KJ mol⁻¹) in LA136D have higher bonding energy than C-C (347 KJ mol⁻¹) and C-H (411 KJ mol⁻¹), which mainly presence in PVDF and SBR, also contributes to reducing volatile fragments at high temperature. The FTIR analysis of the non-volatile residues after 550 °C treatment of LA136D shows the presence of C-O and C-N groups (**Figure 3 (c)**). It verifies that polyacrylonitrile and poly (methyl acrylate) is the key to the low ψ of LA136D. In addition, LA136D shows a low thermal decomposition rate in comparison with PVDF and SBR, as shown in **Figure 3 (b)**. The slow mass reduction of LA136D as the temperature increase indicates a step-by-step decomposition of the molecule groups. This is due to the reasonable setting of thermal hypo-stable groups (C-N, C-C, C-H) and thermal stable groups (C[?]N, C=O) which have a different T_o . The low thermal decomposition rate means a low released rate of gas fragments in binder thermal decomposition, this is especially important to maintain electrode mechanical integrity in TBs operation as will be proved in the next part.

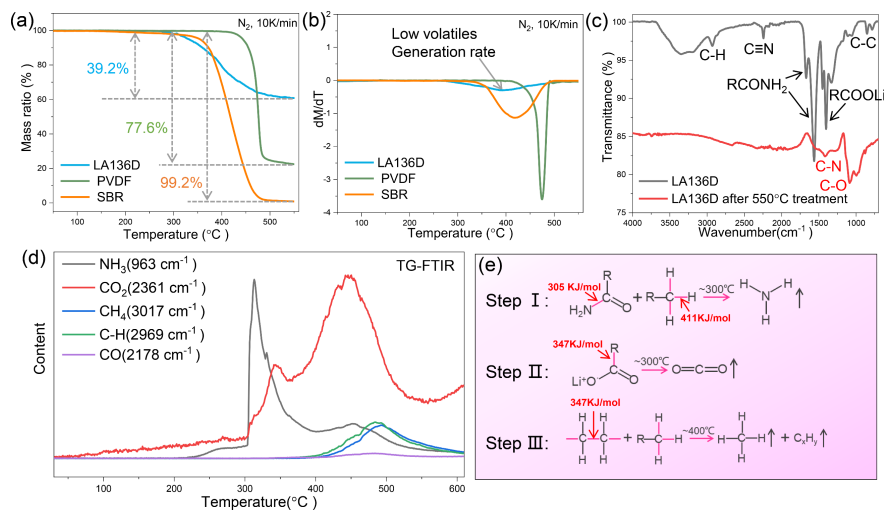


Figure 3. The thermal properties of acrylic acid derivative terpolymer. (a) The thermal gravimetric (TG) curves of LA136D, PVDF, and SBR, the proportions of volatiles generated in the three binders thermal decomposition are 39.2wt %, 77.6wt % and 99.2wt % respectively; (b) the differential coefficient of the TG curves in (a), it is shown LA136D has the lowest volatiles generation rate in the thermal decomposition; (c) the Fourier-transform infrared spectroscopy (FTIR) results of LA136D before and after 550 °C treatment, it is shown there are some C-N and C-O groups in the solid residues, which indicates C[?]N and C=O are beneficial to reach a low volatile proportion in thermal decomposition; (d) the in-situ analysis of the gaseous fragments produced in LA136D thermal decomposition by using TG-FTIR; (e) The proposed thermal decomposition process of LA136D at the high temperatures.

To further study the thermal decomposition process of LA136D, we studied the gas products of LA136D by TG-FTIR. The result is shown in **Figure 3 (d)**. It is shown that few NH₃ occur at about 230 degC

and spurts out after 300 degC, indicating the breaking of C-H (possibly the ends of the main chain) and C-NH₂. At the same time, the CO₂ generates at nearly 300 degC, indicates the breaking of R-COOLi (the occurrence of CO₂ before 300 degC is due to the background of TG-FTIR). The CH₄ and other C-H volatiles occur after 400degC, referring to the break of the -C-C- chain, this can also be verified by the differential curve of LA136D in Figure 3 (b) whereas the rate of thermal decomposition reaches peak value. Based on the discussions above, the thermal decomposition process and the gas products of LA136D can be described in **Figure 3 (e)**. When heating the LA136D, RCO-NH₂ and R-COOLi begin to break at nearly 230 degC and 300 degC accompanying the generation of NH₃ and CO₂ gaseous respectively. The RCO-NH₂ breaking rate reaches a peak value at 320 degC. As the temperature keeps increasing to 400 degC, the main chain -C-C- begins to break and CH₄ or other C-H gaseous fragments are produced. The break of R-COOLi goes with the whole heating process.

2.3. The adhesion strength of acrylic acid derivative terpolymer

Due to most of the binders being non-electrochemical active and non-electronic conductivity, it is desirable to develop binders with high adhesion capability to reduce the addition content (χ) in the electrode to reach high electrochemical performance. As regards TBs, this is more important because the gas production of binders in thermal decomposition at TBs operation temperature may lead to the break of the battery bulk. LA136D is known for its excellent adhesion strength and is used in silicon and sulfur electrode manufacturing in secondary batteries.^[29,30] In contrast to the traditional PVDF binder, which interacts with electrode materials via weak Van der Waals forces, LA136D interacts with electrode materials via covalent bonds.^[31] The large amounts of high polarity groups (-C[?]N, -COONH₂, and -COOLi) in the side chain of LA136D act as the adsorption points to bond the electrode materials and current collector. In this work, we fabricated TBs thin film electrode by using LA136D as the binder and studied the electrode adhesion capability through an electrode peel-off test. **Figure 4 (a)** shows the preparation process of slurry coating and **Figure 4 (b)** is the prepared thin film cathode. **Figure 4 (c)** is the schematics of the electrode peel-off test process. **Figure 4 (d)** shows the peel-off force used to peel the different electrodes. For comparison, we also studied the electrode adhesion ability fabricated by PVDF and SBR. The content of the different binders in the electrode is kept to the same (1wt %), and the electrode thickness is controlled at 100 μ m and with similar tap density (~ 3.5 mg cm⁻³). From Figure 4 (d), LA136D shows the highest peel-off force of 140 N, SBR shows a medium peel-off force of 98 N, and PVDF shows the lowest peel-off force of 60 N. The peel-off test indicates LA136D is capable to fabricate a mechanically robust electrode even at a low content. **Figure 4 (e)** is the digital pictures of electrodes after the peeling test. It can be seen that LA136D electrodes have the best surface integrity. This result is consistent with the peel-off force.

Traditional pressed-pellet technology is hard to produce electrodes with non-circular shapes and restricts the shape-accommodation capability of TBs.^[32] Herein, it is shown that LA136D thin film electrode can be cut into various shapes randomly, as shown in **Figure 4 (f)**. In addition, the LA136D electrode also shows excellent handling properties (**Figure 4(g)**). The electrode materials do not drop even at a high crinkle angle. It is worth noting that the content of LA136D used in the electrode is 1wt %. The “sticky” property of LA136D can be observed visibly in **Figure 4 (h)**, it is consistent with the high bonding capability of LA136D that few LA136D can bond to electrode materials efficiently through the high polarity groups.

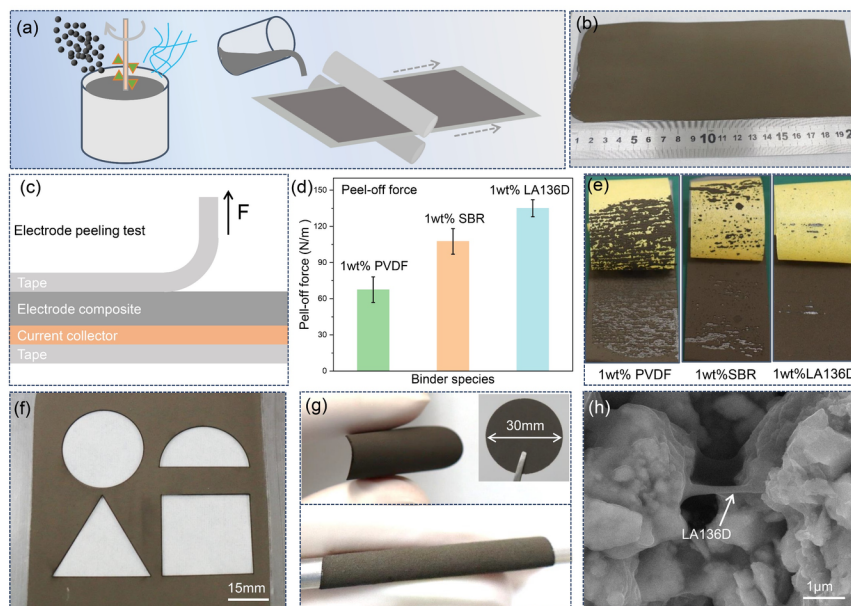


Figure 4. The characterization of adhesion strength of acrylic acid derivative terpolymer. (a) The schematics of the fabricating process of slurry coating; (b) the digital picture of Fe_{0.5}Co_{0.5}S₂ thin film cathode prepared by LA136D; (c) the schematics of electrode peel-off test; (d) the peel-off force of electrodes with a different binder, the content of the binders in the electrodes are 1wt %, the electrode thickness is about 100 μm, the tape density of different electrodes is controlled at 3.5 mg cm⁻³; (e) the digital pictures of electrodes after peel-off test; (f) the digital picture of LA136D thin film electrode after being cut into different shapes, it is shown that the electrode maintains excellent mechanical integrity and without any powder materials drop after cut; (g) the demonstration of the mechanical properties of LA136D thin film electrode, LA136D electrode shows no electrode powder materials drop even at a high curvature; (h) the SEM picture of LA136D electrode, it indicates that small dots of LA136D can bond the electrode powders efficiently.

2.4. The study of the electrochemical performance of thin-film thermal batteries

The low χ and low ψ of LA136D contribute to manufacturing thin film cathodes with low volatility. Herein, we studied the LA136D thin film electrode electrochemical performance in both thermal battery single cells and stacks and verified the volatility of the electrode. **Figure 5 (a)** is the schematics of equipment used for thermal battery single-cell discharge. The single cell consists of a cathode, separator, and anode set between the two-heating plate. The temperature used to heat the single cell is 500 °C and the stress is 20 N cm⁻². **Figure 5 (b)** are the discharge curves of single cells assembled by LA136D thin film cathode and traditional pellet cathode. It is shown that LA136D thin film cathode has a discharge capacity of 1360 As g⁻² at 0.2 A cm⁻². In contrast, the value is 1170 As g⁻² for the pellet cathode. In addition, LA136D thin film cathode shows smaller polarization (~0.5 V) in comparison with the pellet electrode. Combined with the discharge capacity and voltage platform, LA136D thin film cathode shows a 22% energy density increase. **Figure 5 (c)** shows the pulse properties of single cells with different cathodes. It indicates that the internal resistance of the LA136D cell is only 17 mΩ upon 1 A cm⁻² pulse test (The internal resistance is calculated according to $R = (U_2 - U_1) / (I_2 - I_1)$). In contrast, the internal resistance of the pellet cell is 75 mΩ, which is about four times higher than the LA136D cell. The superior discharge capacity and pulse performance indicate the superiority of the LA136D thin-film cathode to the traditional pressed-pellet thick cathode and prove that the LA136D binder is compatible with TBs cathode and molten electrolyte materials.

Furthermore, to verify the volatiles that produced in the thermal decomposition of LA136D do not bring

safety risks to TBs, we studied the performance of the LA136D thin film cathode in the real hermetically sealed TBs stacks. **Figure 5 (d)** is the schematics of thermal battery stacks assembled in this study. The batteries include 40 single-cells in the series and 41 pyrotechnic pellets, the pyrotechnic pellets are positioned between cells and the two ends of the stacks. The thickness of the LA136D thin film cathode used in assembling thermal battery is 200 μm (100 μm electrode+100 μm current collector). For comparison, a 300 μm +100 μm pellet cathode is also used to assemble the thermal battery stack. The diameter of both electrodes is 60 mm. The thermal design of the two thermal batteries is kept the same, namely, the highest temperature of the two thermal batteries is the same. The height of the thin film thermal battery and pellet thermal battery stack is 45.4 cm and 60.6 cm respectively. Thin-film thermal battery reduces about 25% height in comparison with pellet thermal battery. The height difference directly affects the activation time of the thermal battery. The activation time is extraordinarily important for military and emergency power sources because it directly relates to the response time in emergency accidents. **Figure 5 (e)** is the activation voltage curves of thermal batteries. The thin film thermal battery spends about 395 mS to reach 80 V working voltage, which is 38% faster than the pellet thermal battery. This means LA136D thin film cathode is more suitable to construct rapidly-activation thermal batteries. **Figure 5 (f)** are the 130 s pulse test results of the different thermal batteries. Consistent with single-cells, LA136D thin film cathode shows superior discharging capacity at big current density which indicates LA136D thin film is beneficial to construct high power thermal battery. When the TBs have a working time of approximately 100 seconds, the utilization efficiency of cathode materials of the thin-film cathode is three times higher than that of the pressed-pellet cathode. **Figure 5 (g)** is the schematics of the pressure and temperature test of the TBs. To reach the real-time temperature and pressure, a temperature and pressure sensor is put into the thermal battery. The temperature sensor is put on the stack's side surface and the pressure sensor is put at the ends of the stacks. To examine the thermal battery in a rigorous state, thermal batteries are open circuits after activation without load.

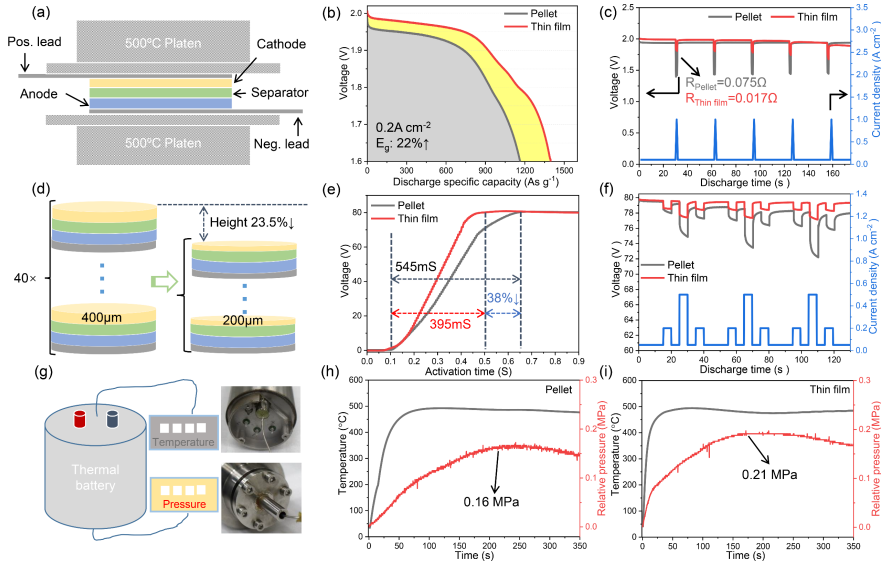


Figure 5. The electrochemical performance of thermal batteries with LA136D thin film electrode. (a) The schematics of the equipment used for thermal batteries single-cell discharge, the heating temperature is 500 °C and the compress is controlled at 20 N cm⁻²; (b) the comparison of the discharge specific capacity and energy density between LA136D thin film cathode and pellet cathode in single-cell configuration, the thickness of electrochemical materials is 100 μm and 300 μm respectively for thin-film and pellet cathodes, the diameter of the cathode is 60 mm, the cathode materials and molten electrolyte used in this experiment are $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$ and LiCl-KCl ; (c) the comparison of pulse discharge performance of thermal batteries with LA136D thin film cathode and pellet cathode; (d) the comparison of the stacks height of

thermal batteries with LA136D thin film cathode and pellet cathode; (e) the comparison of activation time of thermal batteries with different cathodes; (f) the comparison of pulse discharge performance of thermal battery stacks with different cathodes; (g) the illustration of the equipment and method used to detect the internal temperature and pressure of the thermal batteries, the results are shown in (h) and (i) respectively.

Figure 5 (h) and (i) are the temperature and pressure curves of thermal batteries after activation. Due to the smaller height, the temperature increase in the thin film thermal battery is faster than the pellet. The P is directly related to temperature and the amount of gases in binder thermal decomposition. The pressure increase in the thin-film thermal battery is faster than the pellet due to the faster rate of temperature increase. The gases produced by binder decomposition also contribute to the fast increase of gas pressure in thin-film thermal batteries. The highest relative pressure after activation is 0.16 MPa and 0.21 MPa respectively for the thin-film and pellet thermal batteries which indicates LA136D only produces 0.05 MPa gases in the thermal battery. The internal gas pressure of the LA136D thermal battery is less than the safety threshold (0.3 MPa) which we simulate in the previous, indicating that the LA136D does not lead to any distortion of TBs bulk. Therefore, we have shown LA136D will not bring safety risks to the thermal battery stacks and will not detriment the electrochemical performance due to the minim addition.

Excepting for the gas pressure increment, the gas released in binder thermal decomposition may deteriorate the electrode integrity, as shown in **Figures 6 (a) and (b)**. A binder with a low gas production rate in thermal decomposition is beneficial to maintain the mechanical integrity electrode while a binder with a high gas production rate is bad for the electrode's mechanical integrity. To verify the mechanical integrity of the LA136D thin film electrode in TBs operation, we disassembled the thermal battery stack after discharge. **Figure 6 (c)** is the digital picture of the LA136D thin film cathode after discharge. It can be seen that the thin film electrode maintains well integrity even after discharging at high temperatures, and without any powdered materials drop. The cross-section of the discharged single cell also shows a regular morphology (**Figure 6 (d)**). These results prove that LA136 is capable to maintain mechanical integrity in TBs operation. In contrast, a thin-film cathode prepared by PVDF binder shows many cracks after discharge.

Figure 6 (e) is the comparison of the reported binder used in fabricating thermal battery thin film cathodes in the aspects of χ and ψ . It can be found LA136D have the lowest χ and ψ . Such properties enable LA136D to fabricate thin-film cathodes with low volatility and high electrochemical performance.

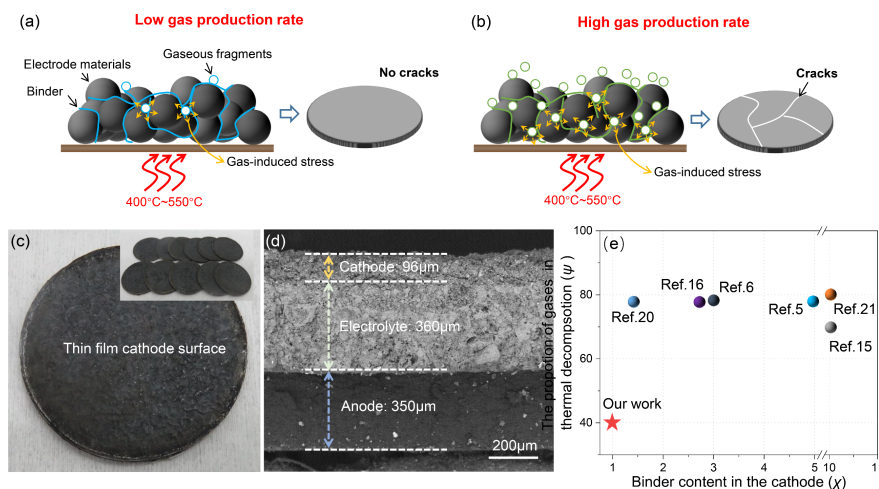


Figure 6. The illustration of mechanical integrity of LA136D thin-film cathodes at high temperatures. (a) and (b) are the schematics of slurry-coated cathodes experienced in the high-temperature environment, binder with a low gas production rate in thermal decomposition is beneficial to maintain the mechanical integrity in TBs operation (a), while a binder with a high gas production rate always leads

to electrode cracks (b); (c) the digital picture of LA136D thin film cathode after discharging, it shows an integrity electrode surface; (d) the cross-section of LA136D single-cell after discharging; (e) the comparison of ψ and χ of binder in the recent slurry-coating works.

3. Conclusions

We fabricated a 100 μm thin-film cathode for TBs by using an acrylic acid derivative terpolymer (LA136D) binder and studied the performance in both single-cells and stacks. It is found the ψ of LA136D is relatively low (39.2wt %). And due to the high adhesion strength, LA136D can fabricate thin-film, non-circular, and mechanical robust electrodes at a content of 1wt %, which contributes to only 0.05 MPa gas pressure increase in real hermetically sealed thermal battery stacks. The single-cell and stacks electrochemical performance tests are shown LA136D is well compatible with the cathode and molten salt materials, and the LA136D thin-film cathode exhibits superior electrochemical performance to the traditional pressed-pellet cathode. Especially, in a 130s pulse discharging test, the TBs it is indicated that LA136D thin-film cathode leads to a remarkable 440% reduction in polarization and 300% enhancement in the utilization efficiency of cathode materials, while with only $\sim$ 0.05 MPa gas pressure increment compare with the traditional pressed-pellet cathode. Our work proves the feasibility of LA136D in fabricating safe thin-film cathodes for high-efficiency and high-power TBs and contributes to arousing the attention to gas production of binders in real thermal battery stacks.

4. Experimental Section

Materials and electrode preparation: the acrylic acid derivative terpolymer (LA136D, Chengdu Indigo, China), polyvinylidene fluoride (PVDF) binder (Arkema, HSV900), butadiene-styrene rubber (SBR) emulsion (JSR, 104A), $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$, LiCl-KCl molten electrolyte and LiB alloy were commercially available and used as received. The LA136D-based cathode slurry was prepared by mixing LA136D and $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$ cathode materials in a planetary centrifugal mixer and stirred for 1.5 h, the mass ratio of LA136D and $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$ is controlled at 1:99. The same procedure and material ratio are applied in PVDF and SBR cathode slurry. The slurry was coated on graphite paper current collector (100 μm) by blade casting. The electrode mass loading was controlled at 35 mg cm^{-2} by adjusting the casting thickness and solid content of the slurry. The thin film electrode thickness after the calendar is about 100 μm . The contrast pellet electrode was prepared by pressed-pellet technology with a thickness of 400 μm (including 100 μm graphite paper current collector).

Binder and thin film electrode characterization: the thermal properties testing was conducted on a thermal analysis system with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ from 30 degC to 1000 degC in N_2 . The Fourier Transform Infrared (FTIR) spectroscopy test of LA136D before and after 550 degC treatment is conducted by using Attenuated Total Reflection (ATR) model. The gaseous products of LA136D were conducted on TG-FTIR with a heating rate of 10 degC min^{-1} from 30 degC to 600 degC in N_2 . The electrode peeling test was conducted. The microstructure morphology was observed by SEM.

Electrochemical performance characterization: the thermal battery single cells were assembled by using a pellet cathode and thin film cathode respectively. The cathode material is $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$, the molten electrolyte is LiCl-KCl, and the anode material is LiB alloy. The compressed pressure used for cell construction is about 0.5 t cm^{-2} . The single cells discharge test was conducted in an Ar_2 atmosphere environment, with a temperature of 500 degC and with a compress of 20 N cm^{-2} . The discharge was conducted by a LAND battery test system (Wuhan LAND, China). The current used for single cells capacity characterization is controlled at 0.2 A cm^{-2} and the cut-off voltage is 1.6 V. The pulse discharge was conducted with a consistent current density of 0.1 A cm^{-2} and a pulse current density of 1 A cm^{-2} . The thermal battery stacks was assembled in a dry air room and a pulse discharge pattern of 0.05 A cm^{-2} (15s)-0.2 A cm^{-2} (5s)-0.05 A cm^{-2} (5s)-0.5 A cm^{-2} (5s)-0.05 A cm^{-2} (5s)-0.2 A cm^{-2} (5s).

Thermal battery inner temperature and pressure characterization: the column thermal battery stainless steel shell was pre-processed with two holes on the ends for signal transfer. The temperature sensor was set on the thermal battery stack surface and can work normally at 600 degC. The pressure sensor was put at the ends

of the column thermal battery, outside the insulation layer. The holes were sealed by a high-temperature ceramic binder after the battery assembly.

Supporting Information

Supporting Information is available from the Wiley Online Library or the author.

Acknowledgment

The authors are grateful for the support from the China Academy of Engineering Physics and the National Natural Science Foundation of China (NSFC-No. 52102319, 12104422, U1930208).

Conflict of Interest

The authors declare no conflict of interest.

References

1. ASB corporation home page, <https://www.asb-group.com/>, accessed: 7, 2023.
2. Eaglepicher corporation home page, Thermal batteries. <https://www.eaglepicher.com/products/thermal-batteries/>, 7, 2023.
3. R. A. Guidotti, P. Masset, *J. Power Sources* **2006**, *161* (2), 1443-1449.
4. J. Ko, S. H. Kang, H.-W. Cheong, Y. S. Yoon, J. Ko, S. H. Kang, H.-W. Cheong, Y. S. Yoon, *Journal of the Korean Ceramic Society* **2019**, *56* (3), 233-255.
5. J. Ko, I. Y. Kim, H. Cheong, Y. S. Yoon, *J. Am. Ceram. Soc.* **2017**, *100* (10), 4435-4441.
6. J. Ko, I. Y. Kim, H. M. Jung, H. Cheong, Y. S. Yoon, *Ceram. Int.* **2017**, *43* (7), 5789-5793.
7. C. A. Apblett, Sandia National Lab. (SNL-NM), Albuquerque, NM (United States): 2016.
8. E. Allcorn, G. Montoya Nagasubramanian, B. M. Height, H. E. Apblett, C. A. Anderson, T. M., Sandia National Lab.(SNL-NM), Albuquerque, NM (United States): 2018.
9. D. V. Kumar, D. Joshi, Fuze Power Supply Systems, *ARDE Technical* .
10. R. Guidotti, S. Preston, In *Electrode fabrication processes for thermal batteries* , 5th International Energy Conversion Engineering Conference and Exhibit (IECEC), 2007, p4706.
11. T. Leviatan, In *Development of thin layer electrochemical components for advanced thermal batteries* , 9th Annual International Energy Conversion Engineering Conference, 2011, p6005.
12. T. D. Manh, T.-T. Tan, J.-K. Chang, *Journal of Materials Research and Technology*, **2021**, *13* , 1139-1149.
13. Y. S. Zhang, N. E. Courtier, Z. Zhang, K. Liu, J. J. Bailey, A. M. Boyce, G. Richardson, P. R. Shearing, E. Kendrick, D. J. Brett, *Adv. Energy Mater.* **2022**, *12* (2), 2102233.
14. E. Kendrick, Advancements in manufacturing. In *Future lithium-ion batteries* , 2019, pp262-289.
15. F. M. Delnick, F. W. Reinhardt, J. G. Odinek, US Patent 7947397, 2011.
16. Z. Liao, L. Fu, J. Zhu, W. Yang, D. Li, L. Zhou, *J. Power Sources* **2020**, *463* , 228237.
17. I. Oh, J. Cho, K. Kim, J. Ko, H. Cheong, Y. S. Yoon, H. M. Jung, *Energies* **2018**, *11* (11), 3154.
18. F. C. Krieger, M. S. Ding, ARMY RESEARCH LAB ADELPHI MD SENSORS AND ELECTRON DEVICES DIRECTORATE, 2015.
19. I. Y. Kim, S. P. Woo, J. Ko, S.-H. Kang, Y. S. Yoon, H.-W. Cheong, J.-H. Lim, *Frontiers in Chemistry* **2020**, *7* , 904.

20. J. Hu, Y. Chu, Q. Tian, J. Wang, Y. Li, Q. Wu, L. Zhao, Y. Zhu, *Mater. Lett.* **2018**, *215* , 296-299.
21. L. H. Gaabour, *J. Mater* **2015**, *2015*(82485910.1155), 2015.
22. F. M. Delnick, US Patent 8460823, 2013.
23. C. L. Beyler, M. M. Hirschler, *SFPE handbook of fire protection engineering*, **2002**, *2* (7), 111-131.
24. K. S. Lau, *Handbook of thermoset plastics* , Elsevier, 2014, pp 297-424.
25. P. Kori, B. H. Vadavadagi, R. K. Khatirkar, *Materials Today: Proceedings* **2020**, *28* , 1895-1898.
26. C. Huang, H. Yang, Y. Li, Y. Cheng, *Anal. Lett.* **2015**, *48* (13), 2011-2021.
27. M.-H. Yang, *Polym. Test.* **2000**, *19* (1), 105-110.
28. S. Madorsky, S. Straus, *J. Res. Natl. Bur. Stan* **1954**, *53* , 361.
29. Tao Y., Wei C., Fei H., An Y., Tian Y., Wei H., Xiong S., Feng J., *J. Power Sources* **2020**, *455* , 227967.
30. Tao Y., Tian Y., An Y., Wei C., Li Y., Zhang Q., Feng J., *Sustainable Materials and Technologies* **2021**, *27* , 00238.
31. J. T. Li, Z. Y. Wu, Y. Q. Lu, Y. Zhou, Q. S. Huang, L. Huang, S. G. Sun, *Adv. Energy Mater.* **2017**, *7* (24), 1701185.
32. J. R. Sweeney, I. McKirdy, R. Comrie, I. Stewart, Some advances in the application of thermal battery technology, *ASB Group, www. asb-group. com*, **2004** .

Supporting Information

Low-volatile binder for safety slurry-coated thin-film cathodes of high-efficiency and high-power thermal batteries

Yong Xie^{1*}, Xu Zhang¹, Liangping Dong¹, Yong Cao¹, Xiaojiang Liu¹, Yixiu Cui¹, Chao Wang^{1*}, Yanhua Cui^{1*}, Xuyong Feng², Hongfa Xiang², and Long Qie³

¹Laboratory of Electrochemical Power Sources, Institute of Electronic Engineering, China Academy of Engineering Physics, Mianyang, Sichuan 621000, China

²School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, Anhui, China

³State Key Laboratory of Material Processing and Die & Mold Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

*Corresponding authors

Email address: yongxie@caep.cn

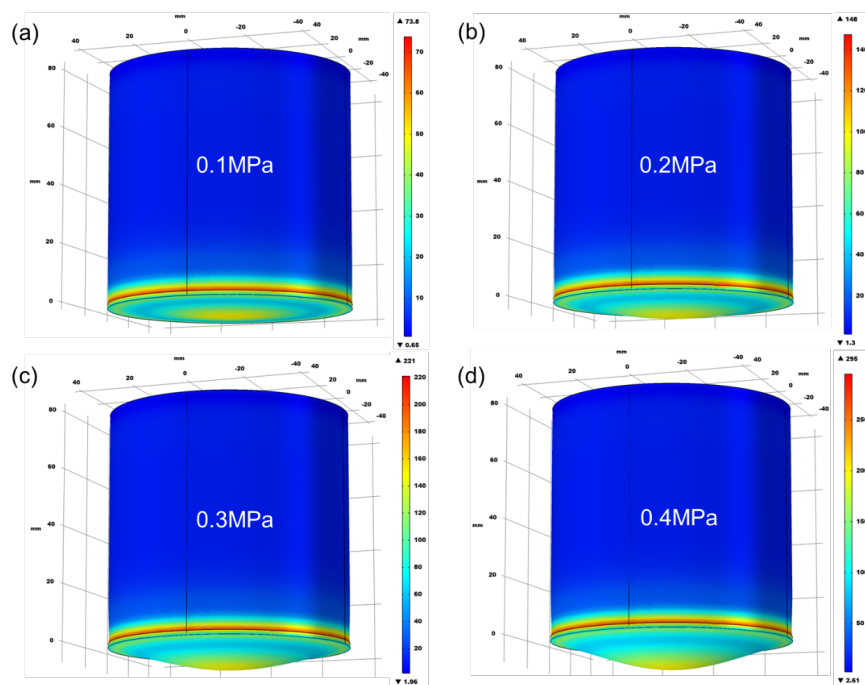


Figure S1. The simulation of the Von Mises Stress brought to a thermal battery stainless steel shell under different internal gas pressure.