Recent Progress in Cathode Materials for Thermal Batteries

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ABSTRACT

Thermal batteries are reserve batteries with molten salts as an electrolyte, which activates at high temperature. Due to their excellent reliability, long shelf life, and mechanical robustness, thermal batteries are used in military applications. A high-performance cathode for thermal batteries should be considered in terms of its high capacity, high voltage, and high thermal stability. Research progress on cathode materials from the recent decade is reviewed in this article. The major directions of research were surface modification, compounding of existing materials, fabrication of thin film cathode, and development of new materials. In order to develop a high-performance cathode, a proper combination of these research directions is required while considering mass production and cost.

Key words : Thermal batteries, Cathode materials, High capacity, High voltage, High thermal stability

1. Introduction

Thermal batteries are reserve batteries that can be stored for a long period in an inactive state, which can then be activated to generate power when needed. Thermal batteries include molten salts as an electrolyte and employ an internal pyrotechnic source to bring the battery stack to the operating temperature. Thermal batteries are high-temperature power sources that typically operate between 350 and 550°C. Thermal batteries are used for many military applications, such as power sources for guided missiles and proximity fuses in ordnance devices because of their excellent mechanical robustness, reliability, and long shelf life¹⁾. The progress of research on thermal batteries until about 2006 is summarized in the review by Masset *et al.*¹⁻⁵⁾ This review provides an overview of molten salt electrolytes,²⁾ cathode materials,^{3,4)} and molten salt electrolytes⁵⁾ of thermally activated batteries. As a representative thermal battery electrode, Li-Si is used as an anode and FeS₂ (pyrite) is used as a cathode; LiCl-KCl is used as an electrolyte. Fig. 1 shows the basic structure of an Li-Si/LiCl-KCl/FeS₂ thermal battery. So far, various studies have focused on optimizing each component in these systems.⁶⁻⁹⁾

Among them, studies focusing on the cathode are largely divided into materials and manufacturing methods. The most commonly used cathode material to date is FeS₂. In addition to studies on optimizing electrode fabrication using

FeS₂,¹⁰⁻¹⁵⁾ studies have been conducted on the use of materials such as CoS₂,¹⁶⁻²¹⁾ NiS₂,²²⁻²⁴⁾ NiCl₂,²⁵⁻²⁸⁾ CuVO,²⁹⁻³⁰⁾ and others.³¹⁻³³⁾ Masset *et al.* cited the following key properties to be considered as cathode materials for thermal batteries:⁴⁾

- Redox potential: it should have a discharge potential that is compatible with the electrochemical window of the electrolyte in order to prevent oxidation.
- Ability to provide a fixed discharge plateau: it should undergo multiphase discharge and not intercalation.
- High thermal stability: thermal decomposition and associated possible chemical reactions caused by decomposition products should be minimized (e.g., S₂ in the case of FeS₂ reacting with the anode or pyrotechnic source in the battery).
- Electronically conductive: the resistance of the cathode should be minimized.
- Low solubility of the cathode materials in molten electrolytes: self-discharge reactions with attendant loss in capacity should be prevented.
- Low solubility of discharge products in the molten electrolytes: prevent self-discharge reactions.
- Stable towards moisture and/or oxygen: to prevent oxide production at the cathode surface.
- Ability to be wetted by electrolyte: this minimizes the contact resistance at the electrolyte (separator)/electrode interface.
- Good discharge kinetics (high exchange-current density): provides high rate capability.
- Reasonable costs.
- Being environmentally friendly is an additional desirable attribute.

The second area of focus in prior research is on the method for manufacturing the cathode electrode. Generally,

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Fig. 1. Cross-sectional view of an Li-Si/FeS₂ thermal battery. Reprinted with permission from Ref. [1]. Copyright 2006 Elsevier B. V.

the constituent materials are produced in the form of pellets with a thickness of several hundreds of micrometers using a powder compaction process. However, the formed pellets are thicker than the optimum thickness in terms of utilization of the electrode material because they must maintain a minimum mechanical strength. For these reasons, an electrolyte material is added to the electrode to compensate for the lower utilization of the electrode material. However, this approach makes the electrode becomes thicker and reduces the ratio of the active material in the electrode. When the thickness of the electrode pellet is greater than a certain level, electrode utilization decreases significantly, which may decrease the energy density of the thermal battery. To solve such a problem, it is essential to choose a process for thinning the electrode such that the electrode has sufficient mechanical strength with optimal electrochemical performance. Therefore, some studies focused on the use of a tape casting process to thin the cathode of a thermal battery.¹¹⁻¹³⁾

In this review, the cathode materials of thermal batteries are reviewed in terms of material types and electrode manufacturing methods. The scope of this review is the past 10 years since the reviews published by Masset *et al.*¹⁻⁵⁾

2. FeS₂

The intrinsic difficulties of engineering a thermal battery based on Ca/CaCrO₄ electrochemistry were obviated with the introduction of Li-alloy/FeS₂ couples.¹⁾ The performance of the Ca/CaCrO₄ electrochemical system tended to be somewhat unpredictable.¹⁾ FeS₂ was readily obtained from processing pyrite, which is a plentiful, inexpensive material compared to chemically synthesized CaCrO₄. In addition, FeS₂ has higher electrical conductivity at elevated temperatures. This provides improved power and lifetimes over the Ca/CaCrO₄ system.^{3,4)} For these reasons, the Li-alloy/FeS₂ system is still the most widely used electrode for thermal batteries. However, the performance improvement is limited due to the low thermal stability and low open circuit voltage compared to other materials, and studies have been conducted to supplement these findings.¹⁰⁻¹⁵⁾

Lee *et al.* studied the use of carbon black and carbon nanotubes on an FeS₂ cathode in Li-Si/FeS₂ thermal batteries.¹⁰⁾ Discharge measurements and the calculated total polarization confirmed that the performance of the single cell improved when a carbonaceous material was added (Fig. 2(a, b)). In Fig. 2(c, d), Nyquist plots of data from the FeS₂ cathode are shown for various contents of carbonaceous materials. The impedance of each sample increased as the content increased. The results from a pristine sample were not compared together; therefore, it is difficult to determine

Fig. 2. (a) Single cell discharge results and (b) total polarization values of pristine, 0.1 wt.% CB, and 0.1 wt.% MWCNT samples. (c, d) Nyquist plots for CB-added and MWCNT-added samples. Reprinted with permission from Ref. [10]. Copyright 2013 The Korean Society of Industrial and Engineering Chemistry.

what level of impedance the 1 wt% sample represents. In addition, there is no information on how the impedance results were obtained when the content was more than 1 wt%, as well as the discharge and total polarization results when the content was greater than 0.1 wt%. Nevertheless, attempts were made to improve the performance of battery electrodes using carbonaceous materials,³⁴⁻⁴³⁾ and the effect was confirmed in the FeS_2 cathode of thermal batteries. However, additional validation is required for actual mass production.

Yoon *et al.* fabricated and evaluated a thin cathode using a tape casting method instead of conventional pellet type cathode.¹¹⁾ When producing a pellet with a powder compaction process, the thickness is minimized for mechanical strength, thus powder compaction is not an appropriate process from the perspective of optimizing the battery performance. In this study, tape casting was used to improve the utilization of cathode materials and the dispersion condition, binder type, and content of each material were determined. As shown in Fig. 3(a), a thin cathode with maximum content of FeS_2 and a minimum amount of binder was pre-

pared. Its mechanical strength was maintained even under severe deformation, as shown in Fig. 3(b), and its discharge rate was nearly twice that of the pellet type, as shown in the Fig. 3(c, d). Tape casting was used to overcome the limitation of a manufacturing process of an existing pellet and showed excellent performance.

Thin cathode production using tape casting was also studied from the perspective of the binder material. Jung *et al.* fabricated a high thermo-stable poly(imide-co-siloxane) (PIS) binder for thermal batteries and used it with an FeS_2 thin cathode in tape casting.¹²⁾ The PIS binder is stable up to 400°C and decomposes at 450°C (Fig. 4(a)). Thus, it cannot be used at 500°C, which is the operating temperature of normal thermal batteries, but shows a higher level compared to binder materials in typical secondary lithium batteries.⁴⁴⁻⁴⁸⁾ During discharge, FeS_2 thin cathodes with PIS showed better performance than conventional pellet-type cathodes, and the total polarization was stable. The discharge capacity is lower than the results presented by Yoon *et al.*¹¹⁾ This may arise due to the difference in FeS_2 particle size. The thermal battery is a special cell that operates at

Fig. 3. (a) The contents of substances contained in the thin cathode and pellet type cathode. (b) Photograph of a thin cathode prepared using tape casting. (c) Discharge graphs of the thin cathode and pellet-type cathode. (d) Discharge results of the thin cathode and pellet-type cathode. Reprinted with permission from Ref. [11]. Copyright 2017 Elsevier Ltd and Techna Group S.r.l.

high temperature (500°C), thus the active electrode material must have excellent thermal stability up to 500°C. The thermal stability decreases when the particle size of FeS₂ is reduced to a certain size or less, and the decomposition rate increases at 500°C, which decreases the discharge capacity.

Another approach to the use of binder materials in thin cathode manufacturing using tape casting is to use multi-walled carbon nanotubes (MWCNTs). Yoon *et al.* applied MWCNTs, which have excellent mechanical strength and conductivity, as an alternative to conventional organic binders for the thin cathode of thermal batteries.¹³⁾ Carboneous materials have been extensively studied and used as additives for electrodes in rechargeable Li-ion batteries.³⁴⁻⁴³⁾ Among them, some carboneous materials are used as current collectors and as electrode supports without adding other binder materials.^{34,49-54)} Noda *et al.* showed that electrodes containing 99 wt% of active materials and 1 wt%

CNTs can be produced.³⁴⁾ However, more research is required to obtain stable cycle performance without electrode degradation in rechargeable batteries, where charge/discharge cycles repeat. On the other hand, thermal batteries are the primary batteries with only one discharge, and are more suitable than rechargeable batteries in active material-CNT composites as the electrode. That is, the use of an FeS₂-MWCNT composite is a universal method in battery research, but is a suitable and novel method for manufacturing a thin cathode for a thermal battery. Two studies^{11,12)} related to thin cathode manufacturing with tape casting used organic binders and they were decomposed before reaching the operating temperature of 500°C. The decomposed organic binder material can generate gas that aggravates the performance of the battery, and the residual material can act as a resistor.⁵⁵⁻⁶⁰⁾ To solve these problems, MWCNTs were used as a binder and conductor for the cathode electrode in this study. MWCNTs have better thermal stability than conventional organic binders and show a mass reduction rate of about 5% at 500°C. Fig. 5(a) shows the contents of each type of cathode. The FeS₂-MWCNT composite cathode has a higher content of FeS₂ than the other types. This is an important factor for increasing the energy density. As shown in Fig. 5(b, c), the FeS₂-MWCNTs composite cathode exhibits higher capacity than the cathode with an organic binder of the same thickness. In this study, MWCNTs are added as a binder in a small amount compared to an organic binder and act as a conductor.

All three of the aforementioned studies¹¹⁻¹³⁾ focus on thin cathode manufacturing methods using tape casting. These are new attempts in terms of manufacturing methods to maximize the performance of thermal batteries based on the material properties of FeS₂. That is, it is meaningful to maximize the utilization ratio of the electrode material, which is poor in the production of the conventional pellet-type material, by manufacturing the electrode with the optimum thickness form an electrochemical perspective. Thin cathode manufacturing is possible with tape casting or with any other method capable of producing films with an appropriate thickness, such as spraying⁶¹⁻⁶⁵⁾ or screen-printing.⁶⁶⁻⁷⁰⁾ Rather, the key to thin cathode manufacturing is high performance, stable, highly productive slurry manufacturing technology.⁷¹⁻⁷⁴⁾ Of course, thin cathode manufacturing technology is applicable not only to FeS₂ but also to other cathode materials. For this purpose, it is necessary to study the binder, solvent, and dispersant suitable for each cathode material.

3. CoS₂ and Bimetallic (Fe-Co) Disulfides

CoS₂ has a lower solubility in molten electrolytes and much higher electronic conductivity, which permits a higher discharge rate. Most importantly, it has a much higher thermal stability and decomposes only above 650°C, which is ~100°C higher than for FeS₂, facilitating its long-term application. However, the major disadvantage of CoS₂ rela-

Fig. 4. (a) Schematic view of the FeS_2 /poly(imide-co-siloxane) composite cathode. (b, c) Discharge capacity and total polarization of the FeS_2 /PIS thin cathode and pellet type cathode. (d) TGA data. (e, f) SEM images of the thin cathode and pellet-type cathode after 1 h treatment at 450°C. Reprinted with permission from Ref. [12]. Copyright: This is an open access article distributed under the Creative Commons Attribution License.

tive to FeS_2 is its higher cost.⁴⁾ Nevertheless, CoS_2 generally has better properties than FeS_2 . For this reason, studies on thermal batteries using CoS_2 cathodes have continued until recently.

Zhu *et al.* fabricated CoS_2 thin cathodes using a screen-printing method and confirmed its feasibility.¹⁶⁾ This study was conducted in the same context as the aforementioned FeS_2 cathode fabricated as a thin film type using tape cast-

Fig. 5. (a) Content of substances contained in the cathodes. (b) Discharge graphs of the cathodes. (c) Discharge results of the cathodes. Reprinted with permission from Ref. [13]. Copyright 2017 The American Ceramic Society.

ing.¹¹⁻¹³⁾ That is, a method for optimizing the thickness in order to maximize utilization of the electrode material was used. A CoS₂ cathode material and screen-printing method were used. Screen-printing is widely used in the textile and electronics industries, and it is a remarkably simple and reproducible production method. In other words, applying this method to thin cathode fabrication for thermal batteries is an appropriate choice. However, this study seems to have a problem in selecting the binder material. In this study, PVDF, which is widely used in the production of electrodes for lithium ion batteries, is used to prepare slurries for screen-printing. However, because the melting point of PVDF is about 160°C, it is not suitable for use in thermal batteries with operating temperatures of approximately 400 to 500°C. As shown in Fig. 6(a), a thin cathode was fabricated with a thickness of 50 μm. As shown in Fig. 6(b), the discharge capacity was more than double that of the pellet-type cathode, producing high voltage and low resistance. However, as described in the aforementioned studies using

tape casting,¹¹⁻¹³⁾ it is a natural phenomenon that the utilization rate of the electrode increases to a certain point and the discharge capacity increases when the electrode is thin. In the case of the pellet-type electrode, the thickness of about 500 μm due to the limited mechanical strength, and lost electrode utilization is minimized by adding an electrolyte material. The key points of research for fabricating a thin cathode are 1) material selection (e.g., active material, binder, solvent, and dispersant) and 2) manufacturing method (e.g., tape casting, screen-printing, or spraying). With respect to these two issues, processing methods such as tape casting,^{75,76)} screen-printing,⁷⁷⁻⁸²⁾ and spraying⁸³⁻⁸⁹⁾ have already been sufficiently investigated in other fields. Of course, appropriate equipment modifications are necessary depending on the application, but this is considered less important than material selection. Very high reliability is required because the thermal battery is a special battery that is primarily used for military applications. Therefore, additional studies on material selection are required to demonstrate the performance while being suitable for the application environment.

Liu *et al.* showed that CoS₂/CNTs composites were prepared using a facile, simple hydrothermal growth process for CoS₂ in the presence of CNTs, as a novel approach of synthesizing cathode composites for thermal battery fabrication.¹⁷⁾ The incorporation of CNTs in the synthesized CoS₂ cathode materials effectively improved the electrical conductivity and discharge performance of the resulting cathode. In this study, single cells with a CoS₂/CNTs cathode, an LiCl-KCl electrolyte, and an Li-Si anode were fabricated and evaluated. All components were fabricated into pellet-type materials using a powder compaction process. This study addresses the addition of CNTs to improve the electrochemical properties of pellet-type cathodes, as in the work of Lee *et al.*¹⁰⁾ The difference between them is the type of active material and the method used to add CNTs. In this study, CoS₂ was used as a cathode material and a CoS₂/CNT composite was fabricated using a hydrothermal method. Hydrothermal growth was carried out at 180°C by adding CNTs and CoS₂ raw materials to a CNT dispersion. There is no mention of the advantages of hydrothermal reacting raw materials and electrical additive over conventional mixing methods. Intuitively, when the hydrothermal method is used, the interfacial properties of CoS₂ and CNTs improve and the electrical conductivity and discharge performance of the cathode are expected to increase.⁹⁰⁻⁹²⁾ However, in this study, the content is not shown, and the goal is to compare CoS₂/CNTs with CoS₂. Fig. 7(a) shows that the thermal stability of CoS₂/CNTs and CoS₂ are similar. The low thermal stability of CoS₂/CNTs is due to the addition of small amounts of CNTs. CoS₂/CNTs with thermal stability above 600°C can perform better than FeS₂ or FeS₂/additive composites. The discharge evaluation results show that the CoS₂/CNT cathode exhibited excellent performance in all aspects, such as discharge capacity and resistance. However, as in the case of FeS₂, additional validation experi-

Fig. 6. (a) Photograph and SEM images of a thin film cathode prepared using screen-printing. (b) Discharge curves and (c) resistance changes of the thin cathode and pellet cathode. Reprinted with permission from Ref. [16]. Copyright 2017 Elsevier B. V.

ments are required based on these results.

Liu *et al.* also studied carbon-coated CoS_2 that was fabricated using hydrothermal synthesis.¹⁸⁾ In this work, a carbon-coated CoS_2 composite was prepared using a facile one-pot hydrothermal method with glucose as a carbon source. During the growth of CoS_2 , the glucose molecules were adsorbed and carbonized in situ on the surface of the as-synthesized CoS_2 , and the resulting carbon coating provided improved electrical conductivity and discharge performance to the composite. In addition to improving the electrochemical performance, the carbon coating also improves the stability of CoS_2 in air. In this study, single cells composed of a carbon-coated CoS_2 cathode, an LiCl-KCl electrolyte, and an Li-Si anode were fabricated and evaluated. All components were fabricated into pellet-type materials using a powder

compaction process. The stability of the carbon-coated CoS_2 and bare CoS_2 in air is shown in the XRD and TGA data in Fig. 8(a, b). After 3 months, impure peaks were detected in bare CoS_2 , while the carbon-coated CoS_2 remained pure. In addition, bare CoS_2 decomposition occurred before 400°C after 3 months, while the carbon-coated CoS_2 remained relatively stable. In the discharge evaluation results, the carbon-coated CoS_2 cathode showed excellent performance compared to bare CoS_2 in all aspects, such as discharge capacity and resistance. However, as in the case of CoS_2/CNT composites, additional verification tests are required before beginning mass production.

Yu *et al.* used other approaches to improve the stability of CoS_2 in air. In this work, Fe-doped CoS_2 ($\text{Co}_x\text{Fe}_{1-x}\text{S}_2$) compounds were synthesized and evaluated as cathode materi-

Fig. 7. (a) Thermal stability of CoS₂ and CoS₂/CNTs. (b) SEM image of CoS₂/CNTs. (c) Specific discharge capacity, (d) energy, (e) pulse power, and (f) polarization data from CoS₂ and CoS₂/CNTs. Reprinted with permission from Ref. [17]. Copyright 2016 Elsevier Ltd.

als for thermal batteries.¹⁹⁾ Single cells composed of a Co_xFe_{1-x}S₂ cathode, an LiCl-KCl electrolyte, and an Li-Si anode were fabricated and evaluated. All components were fabricated into pellet-type materials using a powder compaction process. To investigate the stability of Co_xFe_{1-x}S₂ in air, the as-prepared samples were stored in air (25°C, 100% relative humidity) for 7 days. The XRD patterns Fig. 9(a) do not reveal any apparent impurities or secondary phases in the S-FeS₂ sample, illustrating the stability of FeS₂ in air. Obvious diffraction peaks corresponding to CoSO₄·H₂O can be seen as the content of Co increased further, especially for the S-CoS₂. These results reveal that bimetallic disulfide has better stability in air than that of CoS₂. As shown in

Fig. 9(b, c), the bimetallic disulfide sample was superior to CoS₂ in terms of its electrochemical performance, such as its discharge capacity and total polarization. As shown in Fig. 7(d), the discharge capacities of S-CoS₂ and S-Co_{0.7}Fe_{0.3}S₂ distinctly decrease due to formation of a large amount of CoSO₄·H₂O, while the S-Co_{0.3}Fe_{0.7}S₂ still exhibits good discharge capacity. These results indicate that stability in air has a significant impact on the discharge performance of the disulfides. Bimetallic disulfides with suitable Fe content can exhibit stable discharge performance in air.

This approach was also studied by Zhu *et al.*²⁰⁾ This study shows that composite sulfide Fe_{0.5}Co_{0.5}S₂ can be prepared through traditional high-temperature solid-state and liquid

Fig. 8. (a) XRD patterns of fresh products and products that were stored for 3 months. (b) TG curves of CoS_2 and C@CoS_2 after being stored in dry air for 3 months. (c) Discharge capacity, (d) energy, (e) pulse power, and (f) polarization data from CoS_2 and C@CoS_2 . Reprinted with permission from Ref. [18]. Copyright 2017 published by Elsevier Ltd.

phase methods, and this composite can be used as a cathode material in thermal batteries.²⁰⁾ The goal of this study is to improve the poor thermal stability of FeS_2 and the poor stability of CoS_2 in air by applying Fe-Co bimetallic disulfide. In this study, single cells composed of a $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$ cathode, an LiCl-LiBr-LiF electrolyte, and an Li-Si anode were fabricated and evaluated. The cathode was made of thin film using screen-printing, and other components were fabricated into a pellet-type material using a powder compaction

process. PVDF was used as a binder in thin-cathode manufacturing using screen-printing, as in the work of Zhu *et al.*¹⁶⁾ In order to manufacture a thin cathode with high reliability, the application of a heat-resistant binder should be considered. Clearly, one can see in Fig. 10(a) that a liquid-phase-synthesized $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$ sample is purely single-phase while still maintaining a pyrite structure. All diffraction peaks shifted to lower angles than those observed from cubic FeS_2 . As shown in Fig. 10(b), $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$ has better

Fig. 9. (a) XRD patterns of S-Co_xFe_{1-x}S₂ (samples stored in air). (b) Discharge performance and (c) resistance of the Co_xFe_{1-x}S₂ cell. (d) Discharge performance of the S-Co_xFe_{1-x}S₂ cell. Reprinted with permission from Ref. [19]. Copyright: This is an open access article distributed under the Creative Commons Attribution License.

thermal stability compared to FeS₂. Better thermal stability points to a higher utilization rate for electrode materials, which can greatly increase the discharge performance. Fig. 10(c, d) shows the morphology of Fe_{0.5}Co_{0.5}S₂ prepared using solid-state and liquid phase methods. The particle size of the liquid-phase-synthesized Fe_{0.5}Co_{0.5}S₂ is much smaller, which is expected to have a significant impact on discharge performance. In other words, larger specific surface area can greatly decrease electrochemical polarization, thus significantly slowing down the working voltage drop and improving discharge capacity. The discharge evaluation results in Fig. 10(e, f) show this tendency.

Fe_{0.5}Co_{0.5}S₂ cathodes have higher discharge capacity than an FeS₂ cathode, which is due to the improved thermal stability provided by bimetallic Fe-Co. In addition, liquid phase synthesized Fe_{0.5}Co_{0.5}S₂ has a higher discharge capacity than solid-state synthesized Fe_{0.5}Co_{0.5}S₂. This is primarily due to the pure single-phase and small particle size of the aforementioned liquid phase synthesized Fe_{0.5}Co_{0.5}S₂. New approaches to take advantage of each substance, not limited to conventional disulfide cathodes, are very encouraging.

4. NiS₂

The thermal stability of NiS₂ is intermediate between that of FeS₂ and CoS₂, as shown in Fig. 11(a).⁴⁾ The electrochemical performance of NiS₂ in a LiCl-KCl eutectic electrolyte is compared to that of synthetic FeS₂ and CoS₂ in Fig. 11(b). As expected, the voltage response for the cell with the NiS₂ cathode was intermediate between that of the CoS₂ and FeS₂ cells. However, the overall performance of the NiS₂ cathode was similar to that of CoS₂. Because the costs of NiS₂ precursors are much less than those for CoS₂, the similar electrochemical performance motivates the use of NiS₂ for application where CoS₂ might have been used.¹⁻⁴⁾ However, NiS₂ does not provide a cost advantage over FeS₂ and is not attractive enough to offset the high cost in terms of performance. Several studies that expand on this point have been published.

To maximize the performance of NiS₂, Zhou *et al.* fabricated NiS₂ as a nanostructure and evaluated its properties and performance.²²⁾ In this study, single cells composed of a nano-NiS₂ cathode, a LiCl-LiBr-LiF electrolyte, and a Li-B anode were fabricated and evaluated. All components were fabricated into pellet-type materials using a powder compaction process. Nanostructured NiS₂ powders were prepared by ball-milling for 10 to 40 h and subsequently

Fig. 10. (a) XRD patterns on $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$ synthesized using two different methods. (b) Thermal analysis curves. SEM images of (c) $\text{S-Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$ and (d) $\text{L-Fe}_{0.5}\text{Co}_{0.5}\text{S}_2$. (e) Discharge curves for single cells. (f) Pulsed discharge curves and resistance change curves of single cells. Reprinted with permission from Ref. [20]. Copyright 2018 Elsevier B. V.

heating at 400°C for 1 h using carbonyl nickel and sulfur as precursors. The theoretical capacity of NiS_2 is about 870 mAh/g, but the discharge capacity in practical applications is much lower. The sluggish diffusivity of lithium ions in the NiS_2 cathode and low surface area of the bulk electrodes are identified as the primary factors producing poor discharge performance.⁹³ In addition, intermediate phase evolution with low conductivity can reduce the discharge performance.^{94,95} In this study, the ball-milling time was defined as a control parameter to characterize the particle size of

NiS_2 . As shown in Fig. 12(b), the surface area of the 40 h ball-milled NiS_2 is the largest, which can increase the contact area of the electrode and the electrolyte, thereby improving the discharge performance. The discharge capacity of 40 h ball-milled NiS_2 was largest at the discharge curves (0.1 A/cm^2) shown in Fig. 12(c). The discharge curves (0.5 A/cm^2) in Fig. 12(d) show the same tendency in the discharge capacity, but the voltage plateau becomes clearer. This is due to the intermediate phase generated during discharge, and it becomes clearer as the size of NiS_2 particles

Fig. 11. (a) TGA traces for synthetic FeS_2 , CoS_2 , and NiS_2 in argon. (b) Discharge of Li-Si/LiBr-KBr-LiCl/ MS_2 cells at 500°C. Reprinted with permission from Ref. [4]. Copyright 2007 Elsevier B. V.

decreases. That is, if the size of NiS_2 particles is large, the reaction mechanism of NiS_2 does not occur completely. Inferred from the results of this study, the negative influence of the intermediate phase (NiS) becomes stronger when the NiS_2 particles are larger due to the relatively low conductivity of NiS ,⁹⁶ leading to a decrease in discharge performance. In other words, NiS_2 produced rapid intermediate phase evolution, which increased the discharge capacity of the NiS_2 cathode. This mechanism is shown in Fig. 12(a). This study is meaningful for improving the characteristics of the NiS_2 cathode and for interpreting the performance improvement mechanism in various ways.

Zhou *et al.* studied carbon-modified nano- NiS_2 based on the aforementioned nano- NiS_2 results.²³ In this study, single cells composed of a carbon-coated nano- NiS_2 / nano- NiS_2 cathode, an LiCl-LiBr-LiF electrolyte, and an Li-B anode were fabricated and evaluated. All components were fabricated into a pellet-type material using a powder compaction process. Carbon modification is always seen as an effective

method for improving the conductivity and thermal/structural stability of electrodes.⁹⁷⁻¹⁰² In this study, NiS_2 particles were coated with amorphous carbon. Then they accumulated into submicron particles and were connected/fixed by a carbon network. These effects are shown in Fig. 13(e, f), as shown in the TEM image and schematic diagram. The initial decomposition temperature of nano- NiS_2 increased from 400 to 590°C after carbon modification. As shown in Fig. 13(b), the discharge performance improves as the thermal stability increases. In the case of carbon-coated nano- NiS_2 , the discharge capacity at high temperature shows a stable specific capacity up to 600°C near the initial decomposition temperature (Fig. 13(c)). Beyond 600°C, NiS_2 rapidly decomposes and its specific capacity decreases. Carbon modification not only improves the conductivity of the cathode on its own, but it also inhibits the spread of the low conductivity product Li_2S . This effect is reflected in the pulse discharge and resistance results (Fig. 13(d)).

5. NiCl_2

Due to several advantages mentioned above, disulfide-based materials have been used as the cathode in thermal batteries for decades. However, it is difficult for disulfide materials to meet recent demands for high power thermal batteries due to their low thermal stability and low discharge voltage. As a result, research and development on cathode materials (e.g., NiCl_2) other than disulfide-based materials have continued. NiCl_2 has been considered as one promising cathode material for use in thermal batteries thanks to its high relative potential, high current discharge, high specific energy, and low cost. However, its high solubility in molten salt electrolytes causes thermal batteries to short circuit, and its low electronic conductivity results in long activation time, thus NiCl_2 thermal batteries cannot provide electrochemical performance.²⁵

Zhou *et al.* conducted surface modification with a carbon coating to improve the performance of NiCl_2 -based batteries.²⁵ It was confirmed that modification using carbon coating has a positive effect on electrochemical performance of CoS_2 ¹⁸ and NiS_2 .²³ In this study, the solubility of NiCl_2 in the molten salt was evaluated using a contact angle measurement on the NiCl_2 cathode, which could be used to analyze wetting of the LiCl-LiBr-LiF electrolyte. These results indicate that the carbon coating could inhibit NiCl_2 from dissolving into the molten salt (Fig. 14(a)). Single cells composed of carbon-coated nano- NiCl_2 /pure NiCl_2 cathodes, an LiCl-LiBr-LiF electrolyte, and an Li-B anode were fabricated and evaluated. All components were fabricated into pellet-type materials using a powder compaction process. The carbon-coated NiCl_2 thermal batteries exhibited increased specific capacity and increased specific energy compared to that of pure NiCl_2 thermal batteries.

Zhu *et al.* investigated an alternative to the conventional stainless steel substrate for NiCl_2 -based thermal batteries.²⁶ In this study, an NiCl_2 cathode was fabricated by

Fig. 13. (a) TG data from nano-NiS₂ before and after carbon modification. (b-c) Specific capacities of NiS₂ and NiS₂/C at 0.1 A/cm². (d) Pulse discharge and resistances. (e) TEM images of discharge products. (f) Schematic diagram showing carbon modification. Reprinted with permission from Ref. [23]. Copyright 2018 The Royal Society of Chemistry.

but this could be improved by adjusting the viscosity of the NiCl₂ slurry and the screen-printing processing conditions. Furthermore, additional research on Ni foam may be

needed because the porosity of the Ni foam and the shape of the pore can greatly affect the performance of the cathode. The peak voltage of the NiCl₂ cathode using an Ni foam sub-

Fig. 14. (a) Contact angle test. (b-d) Comparison of the electrochemical performance of single-cell thermal batteries with carbon-coated NiCl_2 and pure NiCl_2 cathodes at 480°C and at various current densities. Reprinted with permission from Ref. [25]. Copyright 2017 Elsevier B. V.

strate is about 2.55 V, which is much higher than that of sulfide cathode materials. In addition, the NiCl_2 cathode with a Ni foam substrate has a specific capacity of 684.61 Asg^{-1} with a cut-off voltage of 1.5 V (stainless steel substrate: 299.39 Asg^{-1}). This improvement can be attributed to the lower resistance of the NiCl_2 cathode on the Ni foam substrate (Fig. 15(d)). It is significant that the results from this study can be used to improve the mass productivity of NiCl_2 cathodes by using a metal foam substrate, which can greatly improve the electrochemical performance and screen printing process, making them suitable for mass production. This approach seems to be applicable to other cathode materials besides NiCl_2 , and it is important to consider the selection of suitable metal foams and shapes. In addition, because metal foam is expected to act as a support for the cathode material, it is also necessary to minimize the amount of binder material added to the slurry.

6. Copper Vanadium Oxide

Copper vanadium oxide provides high voltage, high capacity, and high thermal stability. V_2O_5 and CuO were previously evaluated for use as possible cathodes in thermal batteries.²⁹⁾ In addition, the electrochemistry of $\text{Cu}_5\text{V}_2\text{O}_{10}$ was reported by Sakurai *et al.*¹⁰³⁾ and Eguchi *et al.*¹⁰⁴⁾

A series of the $\text{CuO-V}_2\text{O}_5$ oxides, such as CuV_2O_6 , $\text{Cu}_2\text{V}_2\text{O}_7$, and $\text{Cu}_5\text{V}_2\text{O}_{10}$ were synthesized and evaluated as possible candidate cathode materials in high voltage thermal batteries.²⁹⁾ In this study, single cells composed of a copper vanadium oxide cathode, an LiCl-KCl electrolyte, and an Li-Al anode were fabricated and evaluated. All components were fabricated into pellet-type materials using a powder compaction process. In the Fig. 16(a), $\text{Cu}_2\text{V}_2\text{O}_7$ showed lower thermal stability than CuV_2O_6 , but the weight loss was negligible (0.085%) up to 600°C. This is much smaller than the weight loss observed with sulfide cathode materials. A 3.4 V voltage plateau at a current density of 100 mA/g and a 2.5 V voltage plateau at a current density of 310 mA/g were observed during discharge at 525°C. This is a much higher value than was observed with FeS_2 , which

Fig. 15. (a) Photographs of the NiCl_2 cathode. (b) Cross-sectional SEM images of the NiCl_2 cathode. (c) Discharge curves and (d) resistance changes of single cells with NiCl_2 cathodes. Reprinted with permission from Ref. [26]. Copyright 2017 Elsevier B. V.

Fig. 16. (a) TGA curves of CuV_2O_6 and $\text{Cu}_2\text{V}_2\text{O}_7$. Discharge curves of the (b) CuV_2O_6 and (c) $\text{Cu}_2\text{V}_2\text{O}_7$ cathodes. Reprinted with permission from Ref. [29]. Copyright 2012 Elsevier B. V.

has a voltage plateau ranging from 1.5 to 2 V under similar conditions, and is a characteristic that can contribute to increasing the energy density.

Dai *et al.* studied $\text{Cu}_3\text{V}_2\text{O}_8$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$ thin-film cathodes for thermal batteries.³⁰⁾ In this study, single cells composed of a copper vanadium oxide cathode, a high-voltage

Fig. 17. (a) Discharge profile for an LiSi/Cu₅V₂O₁₀ cell. (b) Polarization of an LiSi/Cu₅V₂O₁₀ cell. (c) Discharge profile of an LiSi/Cu₃V₂O₈ cell. (d) Polarization of an LiSi/Cu₃V₂O₈ cell. Reprinted with permission from Ref. [30]. Copyright 2011 The Electrochemical Society.

compatible electrolyte, and an Li-Si anode were fabricated and evaluated. All components were fabricated into pellet-type materials using a powder compaction process. The cathode was also fabricated as a thin film using tape casting in order to facilitate a suitable performance comparison. The high-voltage compatible electrolyte consists of LiPO₃, Li₂SO₄, Li₂CO₃, and LiF. Copper vanadium oxide has higher voltage than sulfide materials; therefore, it is necessary to study the molten salt electrolyte within a suitable voltage window.¹⁰⁵⁾ In this study, the final constant stable open circuit voltage (OCV) is 2.971 V at 500°C. The discharge profile of the Cu₅V₂O₁₀ thin films contains multiple plateaus, similar to what was observed with a pressed film (Fig. 17(a)). The discharge profile of Cu₃V₂O₈ shows a much more obscure phase change than that of Cu₅V₂O₁₀. To determine the cause of these differences, an analysis of the discharge reaction for each substance would be necessary. The specific capacity of a thin film cathode is higher than that of a pressed cathode, regardless of the cathode materials.

Copper vanadium oxide has excellent properties, such as high voltage and high thermal stability, but studies on this material remain lacking. Applying the functional coating or manufacturing method mentioned above and optimizing the material properties may significantly contribute to the development of thermal batteries with high energy density.

7. Other Materials

In addition to the aforementioned materials, other cathode materials for thermal batteries have been studied recently. Irvine *et al.* investigated ZrS₃ as a possible cathode material for use in thermal batteries.³¹⁾ ZrS₃ has a pseudo one-dimensional structure (Fig. 18(a)). In this study, single cells composed of a ZrS₃ cathode, an LiCl-KCl electrolyte, and an Li-Si anode were fabricated and evaluated. All components were fabricated into pellet-type materials using a powder compaction process. A single 1.7 V voltage plateau at a current density of 11 mA/cm² was observed during discharge at 500°C with a capacity of 357 mAh/g. However, these results are inferior to existing sulfide materials, such as FeS₂, CoS₂ and NiS₂. One thing to note is the high thermal stability of 700°C. This study is an early attempt to apply ZrS₃ as the cathode in thermal batteries, thus additional work should focus on improving the performance of these devices.

Irvine *et al.* investigated CoNi₂S₄ as a candidate cathode material for use in thermal batteries.³²⁾ CoNi₂S₄ adopts an inverse spinel structure, as shown in Fig. 18(d). In this study, single cells composed of a CoNi₂S₄ cathode, an LiCl-KCl electrolyte, and an Li-Si anode were fabricated and evaluated. All components were fabricated into pellet-type

Fig. 18. (a) Crystal structure of ZrS_3 . (b) SEM image of a ZrS_3 cathode. (c) Discharge performance of an LiSi/ZrS_3 cell. Reprinted with permission from Ref. [31]. Copyright: This is an open access article distributed under the Creative Commons Attribution License. (d) Crystal structure of CoNi_2S_4 . (e) SEM image of CoNi_2S_4 . (f) Discharge performance of an $\text{LiSi}/\text{CoNi}_2\text{S}_4$ cell. Reprinted with permission from Ref. [32]. Copyright: This is an open access article distributed under the Creative Commons Attribution License.

materials using a powder compaction process. The CoNi_2S_4 cell exhibits two voltage plateaus at 500°C , one at 1.75 V and the second at 1.5 V. The CoNi_2S_4 cell has a specific capacity of 318 mAh/g from 2.58 to 1.25 V OCV. However, these results are inferior to those mentioned above. CoNi_2S_4 shows the thermal stability of 550°C , which is lower than that of FeS_2 ; hence, its application scope becomes even narrower.

It is encouraging that the development of new cathode materials for thermal batteries is ongoing. However, future studies should focus on improving the capacity, thermal stability, and voltage currently required in industry.

8. Conclusions

Thermal batteries are primarily limited to military appli-

Table 1. Summary of Recent Studies on Cathode Materials for Thermal Batteries

	Cathode	Anode	Electrolyte	Cathode type/Thickness (μm)	Specific capacity (A·sec/g)	Discharge temperature (°C)	Cut-off (V)	OCV (V)	Voltage plateau (V)	Thermal stability (°C)	Ref.
1	FeS ₂	Li-Si	LiCl-KCl	Pellet/ -	-	500	1.56	1.9	1.75/ 1.5/ 1.1	580	[10]
2	FeS ₂	Li-Si	LiCl-KCl	Thin film/ 100	1934	500	1.3	2.0	1.75/ 1.4	580	[11]
3	FeS ₂	Li-Si	LiCl-KCl	Thin film/ 100	1283	500	1.3	1.9	1.8/ 1.4	580	[12]
4	FeS ₂	Li-Si	LiCl-KCl	Thin film/ 50	2305	500	1.3	2.0	1.85/ 1.4	580	[13]
5	CoS ₂	Li-Si	LiCl-LiBr-LiF	Thin film/ 50	2092	500	1.25	1.99	1.9/ 1.76	650	[16]
6	CoS ₂	Li-Si	LiCl-KCl	Pellet/ -	791.28	500	1.7	1.84	1.77/ 1.3	650	[17]
7	CoS ₂	Li-Si	LiCl-KCl	Pellet/ -	848.88	500	1.7	1.84	1.78/ 1.3	650	[18]
8	Co _{0.3} Fe _{0.7} S ₂	Li-Si	LiCl-KCl	Pellet/ -	2304	525	1.0	2	1.85/ 1.3	620	[19]
9	Fe _{0.5} Co _{0.5} S ₂	Li-Si	LiCl-LiBr-LiF	Thin film/ 50	1872.89	-	1.25	2.04	2	620	[20]
10	NiS ₂	Li-B	LiCl-LiBr-LiF	Pellet/ -	2858.4	500	0.5	2.2	1.98/ 1.8/ 1.4	400	[22]
11	NiS ₂	Li-B	LiCl-LiBr-LiF	Pellet/ -	2196	500	1.4	2.0	2.0/ 1.6	590	[23]
12	NiCl ₂	Li-B	LiCl-LiBr-LiF	Pellet/ -	2127.6	480	0.8	2.35	2.3/ 1.5	-	[25]
13	NiCl ₂	Li-Si	LiCl-LiBr-LiF	Nickel foam/ 400	684.61	-	1.5	2.55	-	-	[26]
14	CuV ₂ O ₆	Li-Al	LiCl-KCl	Pellet/ 1000	220	525	2.0	3.5	-	600	[29]
15	Cu ₂ V ₂ O ₇	Li-Al	LiCl-KCl	Pellet/ 1000	125	525	2.0	3.5	-	600	[29]
16	Cu ₅ V ₂ O ₁₀	Li-Si	LiPO ₃ , LiSO ₄ , Li ₂ CO ₃ , LiF	Thin film/ 80	1044	500	2.0	2.971	2.5/ 1.75/ 1.5	-	[30]
17	Cu ₃ V ₂ O ₈	Li-Si	LiPO ₃ , LiSO ₄ , Li ₂ CO ₃ , LiF	Thin film/ 80	990	500	2.0	2.971	2.4	-	[30]
18	ZrS ₃	Li-Si	LiCl-KCl	Pellet/ -	1285.2	500	1.0	1.8	1.7	700	[31]
19	CoNi ₂ S ₄	Li-Si	LiCl-KCl	Pellet/ -	1144.8	500	1.25	2.58	-	500	[32]

cations because of their specificity. This closed and specific propensity is reflected in research activities, and the number of published studies is very small compared to studies on general Li ion batteries. Nevertheless, over the past decade, much valuable research has been conducted on cathode materials for thermal batteries. Table 1 summarizes the main results of recent studies. Today, electronics industries in all fields are rapidly developing, and demand for power sources with high energy density is increasing. The military requires a high-performance power source that can power advanced weapons systems. In other words, future thermal batteries require high energy density and high reliability against external stimuli.

High capacity, high voltage, and high thermal stability are the three most important considerations for the development of high performance thermal batteries. There are four major approaches to improve these.

- I. Surface modification: Coating with carbon or other materials to improve the thermal stability or electrical conductivity of conventional cathode materials.
- II. Alloy and compound: Synthesis of alloy or compound materials to improve the thermal stability or specific capacity of conventional cathode materials.
- III. Manufacturing method: Manufacturing of a thin film cathode to overcome the limitations of pellet-type materials formed via powder compaction.

IV. New materials

It would be possible to develop a cathode for high performance thermal batteries by appropriately combining the above considerations.

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