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 life.

The progress of research on thermal batteries until about 2006 is summarized in the review by Masset et al. This review provides an overview of molten salt electrolytes, cathode materials, and molten salt electrolytes of thermally activated batteries. As a representative thermal battery electrode, Li-Si is used as an anode and FeS\textsubscript{2} (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/FeS\textsubscript{2} thermal battery. So far, various studies have focused on optimizing each component in these systems.

Among them, studies focusing on the cathode are largely divided into materials and manufacturing methods. The most commonly used cathode material to date is FeS\textsubscript{2}. In addition to studies on optimizing electrode fabrication using FeS\textsubscript{2} studies have been conducted on the use of materials such as CoS\textsubscript{2}, NiS\textsubscript{2}, NiCl\textsubscript{2}, CuVO, and others. Masset et al. cited the following key properties to be considered as cathode materials for thermal batteries:

- 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., S\textsubscript{2} in the case of FeS\textsubscript{2} 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,
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.

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. The intrinsic difficulties of engineering a thermal battery based on Ca/CaCrO$_4$ electrochemistry were obviated with the introduction of Li-alloy/FeS$_2$ couples. The performance of the Ca/CaCrO$_4$ electrochemical system tended to be somewhat unpredictable. FeS$_2$ was readily obtained from processing pyrite, which is a plentiful, inexpensive material compared to chemically synthesized CaCrO$_4$. In addition, FeS$_2$ has higher electrical conductivity at elevated temperatures. This provides improved power and lifetimes over the Ca/CaCrO$_4$ system. For these reasons, the Li-alloy/FeS$_2$ 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.

Lee et al. studied the use of carbon black and carbon nanotubes on an FeS$_2$ cathode in Li-Si/FeS$_2$ thermal batteries. 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 FeS$_2$ 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...
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, and the effect was confirmed in the FeS\textsubscript{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. 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\textsubscript{2} and a minimum amount of binder was prepared. 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\textsubscript{2} thin cathode in tape casting. 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.

During discharge, FeS\textsubscript{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. This may arise due to the difference in FeS\textsubscript{2} particle size. The thermal battery is a special cell that operates at
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 FeS\(_2\) 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 multiwalled 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. 30) 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 FeS\(_2\)-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 FeS\(_2\)-MWCNT composite cathode has a higher content of FeS\(_2\) than the other types. This is an important factor for increasing the energy density. As shown in Fig. 5(b, c), the FeS\(_2\)-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 studies 11-13) 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 FeS\(_2\). 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 spraying 61-65) 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 FeS\(_2\) 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. CoS\(_2\) and Bimetallic (Fe-Co) Disulfides

CoS\(_2\) 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 FeS\(_2\), facilitating its long-term application. However, the major disadvantage of CoS\(_2\), rela-
tive to FeS$_2$ is its higher cost. 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. This study was conducted in the same context as the aforementioned FeS$_2$ cathode fabricated as a thin film type using tape cast-

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.
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 type cathode, producing high voltage and low resistance.

Table 1. CNTs and CoS₂ 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-
Liu et al. also studied carbon-coated CoS$_2$ that was fabricated using hydrothermal synthesis. 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$_2$ (Co$_x$Fe$_{1-x}$S$_2$) compounds were synthesized and evaluated as cathode materi-
als for thermal batteries. Single cells composed of a $\text{Co}_x\text{Fe}_{1-x}\text{S}_2$ 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. To investigate the stability of $\text{Co}_x\text{Fe}_{1-x}\text{S}_2$ in air, the as-prepared samples were stored in air ($25\,^\circ\text{C}$, 100% relative humidity) for 7 days. The XRD patterns (Fig. 9(a)) do not reveal any apparent impurities or secondary phases in the S-FeS$_2$ sample, illustrating the stability of FeS$_2$ in air. Obvious diffraction peaks corresponding to CoSO$_4$·H$_2$O can be seen as the content of Co increased further, especially for the S-CoS$_2$. These results reveal that bimetallic disulfide has better stability in air than that of CoS$_2$. As shown in Fig. 9(b, c), the bimetallic disulfide sample was superior to CoS$_2$ 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-CoS$_2$ and S-Co$_{0.7}$Fe$_{0.3}$S$_2$ distinctly decrease due to formation of a large amount of CoSO$_4$·H$_2$O, while the S-Co$_{0.3}$Fe$_{0.7}$S$_2$ 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. This study shows that composite sulfide Fe$_{0.5}$Co$_{0.5}$S$_2$ can be prepared through traditional high-temperature solid-state and liquid
phase methods, and this composite can be used as a cathode material in thermal batteries. 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 Fe$_{0.5}$Co$_{0.5}$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. 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 Fe$_{0.5}$Co$_{0.5}$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), Fe$_{0.5}$Co$_{0.5}$S$_2$ has better

![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.](image-url)
thermal stability compared to FeS$_2$. 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$_{0.5}$S$_2$ prepared using solid-state and liquid phase methods. The particle size of the liquid-phase-synthesized Fe$_{0.5}$Co$_{0.5}$S$_2$ 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$_{0.5}$S$_2$ cathodes have higher discharge capacity than an FeS$_2$ cathode, which is due to the improved thermal stability provided by bimetallic Fe-Co. In addition, liquid phase synthesized Fe$_{0.5}$Co$_{0.5}$S$_2$ has a higher discharge capacity than solid-state synthesized Fe$_{0.5}$Co$_{0.5}$S$_2$. This is primarily due to the pure single-phase and small particle size of the aforementioned liquid phase synthesized Fe$_{0.5}$Co$_{0.5}$S$_2$. New approaches to take advantage of each substance, not limited to conventional disulfide cathodes, are very encouraging.

4. NiS$_2$

The thermal stability of NiS$_2$ is intermediate between that of FeS$_2$ and CoS$_2$, as shown in Fig. 11(a). The electrochemical performance of NiS$_2$ in an LiCl-KCl eutectic electrolyte is compared to that of synthetic FeS$_2$ and CoS$_2$ in Fig. 11(b). As expected, the voltage response for the cell with the NiS$_2$ cathode was intermediate between that of the CoS$_2$ and FeS$_2$ cells. However, the overall performance of the NiS$_2$ cathode was similar to that of CoS$_2$. Because the costs of NiS$_2$ precursors are much less than those for CoS$_2$, the similar electrochemical performance motivates the use of NiS$_2$ for application where CoS$_2$ might have been used. However, NiS$_2$ does not provide a cost advantage over FeS$_2$ 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 NiS$_2$, Zhou et al. fabricated NiS$_2$ as a nanostructure and evaluated its properties and performance. In this study, single cells composed of a nano-NiS$_2$ cathode, 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. Nanostructured NiS$_2$ powders were prepared by ball-milling for 10 to 40 h and subsequently...
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. In addition, intermediate phase evolution with low conductivity can reduce the discharge performance. 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 decreases.
This study is meaningful for improving the characteristics of the cathode, an LiCl-LiBr-LiF electrolyte, and an Li-B anode. That is, if the size of NiS decreases. That is, if the size of NiS particles is large, the reaction mechanism of NiS does not occur completely. Inferred from the results of this study, the negative influence of the intermediate phase (NiS) becomes stronger when the NiS particles are larger due to the relatively low conductivity of NiS, leading to a decrease in discharge performance. In other words, NiS produced rapid intermediate phase evolution, which increased the discharge capacity of the NiS cathode. This mechanism is shown in Fig. 12(a). This study is meaningful for improving the characteristics of the NiS cathode and for interpreting the performance improvement mechanism in various ways.

Zhou et al. studied carbon-modified nano-NiS based on the aforementioned nano-NiS results. In this study, single cells composed of a carbon-coated nano-NiS 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. In this study, NiS 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(c, f), as shown in the TEM image and schematic diagram. The initial decomposition temperature of nano-NiS 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, 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 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 Li2S. This effect is reflected in the pulse discharge and resistance results (Fig. 13(d)).

5. NiCl2

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., NiCl2) other than disulfide-based materials have continued. NiCl2 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 NiCl2 thermal batteries cannot provide electrochemical performance.

Zhou et al. conducted surface modification with a carbon coating to improve the performance of NiCl2-based batteries. It was confirmed that modification using carbon coating has a positive effect on electrochemical performance of CoS2 and NiS. In this study, the solubility of NiCl2 in the molten salt was evaluated using a contact angle measurement on the NiCl2 cathode, which could be used to analyze wetting of the LiCl-LiBr-LiF electrolyte. These results indicate that the carbon coating could inhibit NiCl2 from dissolving into the molten salt (Fig. 14(a)). Single cells composed of carbon-coated nano-NiCl2/pure NiCl2 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 NiCl2 thermal batteries exhibited increased specific capacity and increased specific energy compared to that of pure NiCl2 thermal batteries.

Zhu et al. investigated an alternative to the conventional stainless steel substrate for NiCl2-based thermal batteries. In this study, an NiCl2 cathode was fabricated by
screen printing on stainless steel and nickel foam substrates. In addition, LiCl-LiBr-LiF electrolyte and Li-Si alloy anodes were fabricated into pellet-type materials using a powder compaction process. The shape of the NiCl₂ cathode in Fig. 15(a, b) shows that NiCl₂ penetrates the Ni foam. In Fig. 15(b), NiCl₂ does not penetrate to the back of the Ni foam.

Fig. 12. (a) The effect of nano-NiS₂ in a thermal battery. (b) N₂ adsorption-desorption isotherms (inset: BET surface area). Discharge performance of NiS₂ with different ball-milling times at current densities of (c) 0.1 A/cm² and (d) 0.5 A/cm². (e) Pulsed discharge performance. (f) Resistance variation. Reprinted with permission from Ref. [22]. Copyright 2017 Elsevier B. V.
but this could be improved by adjusting the viscosity of the NiCl$_2$ 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 NiCl$_2$ cathode using an Ni foam sub-

Fig. 13. (a) TG data from nano-NiS$_2$ before and after carbon modification. (b-c) Specific capacities of NiS$_2$ and NiS$_2$/C at 0.1 A/cm$^2$. (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.
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$_2$O$_5$ and CuO were previously evaluated for use as possible cathodes in thermal batteries. In addition, the electrochemistry of Cu$_5$V$_2$O$_{10}$ was reported by Sakurai et al. and Eguchi et al.

A series of the CuO-V$_2$O$_5$ oxides, such as CuV$_2$O$_6$, Cu$_2$V$_2$O$_7$, and Cu$_5$V$_2$O$_{10}$ were synthesized and evaluated as possible candidate cathode materials in high voltage thermal batteries. 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), Cu$_5$V$_2$O$_{10}$ showed lower thermal stability than CuV$_2$O$_6$, 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
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 Cu$_3$V$_2$O$_8$ and Cu$_5$V$_2$O$_{10}$ thin-film cathodes for thermal batteries. In this study, single cells composed of a copper vanadium oxide cathode, a high-voltage...
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 LiPO$_3$, Li$_2$SO$_4$, Li$_2$CO$_3$, 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 Cu$_5$V$_2$O$_{10}$ thin films contains multiple plateaus, similar to what was observed with a pressed film (Fig. 17(a)). The discharge profile of Cu$_3$V$_2$O$_8$ shows a much more obscure phase change than that of Cu$_5$V$_2$O$_{10}$. 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 were 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 ZrS$_3$ as a possible cathode material for use in thermal batteries.\(^{31}\) ZrS$_3$ has a pseudo one-dimensional structure (Fig. 18(a)). In this study, single cells composed of a ZrS$_3$ 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/cm$^2$ 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 FeS$_2$, CoS$_2$, and NiS$_2$. One thing to note is the high thermal stability of 700°C. This study is an early attempt to apply ZrS$_3$ as the cathode in thermal batteries, thus additional work should focus on improving the performance of these devices.

Irvine et al. investigated CoNi$_2$S$_4$ as a candidate cathode material for use in thermal batteries.\(^{32}\) CoNi$_2$S$_4$ adopts an inverse spinel structure, as shown in Fig. 18(d). In this study, single cells composed of a CoNi$_2$S$_4$ 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 final constant stable open circuit voltage (OCV) is 2.971 V at 500°C. The discharge profile of CoNi$_2$S$_4$ thin films contains multiple plateaus, similar to what was observed with a pressed film (Fig. 17(a)). The discharge profile of CoNi$_2$S$_4$ shows a much more obscure phase change than that of Cu$_5$V$_2$O$_{10}$. 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 were may significantly contribute to the development of thermal batteries with high energy density.
materials using a powder compaction process. The CoNi$_2$S$_4$ cell exhibits two voltage plateaus at 500°C, one at 1.75 V and the second at 1.5 V. The CoNi$_2$S$_4$ 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$_2$S$_4$ 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-
The military requires a high-performance power source that can power advanced weapons systems. In other words, the demand for power sources with high energy density is increasing. It would be possible to develop a cathode for high performance thermal batteries by appropriately combining the above considerations.

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REFERENCES

1. R. A. Guidotti and P. Masset, “Thermally Activated (“Thermal”) Battery Technology Part I: An Overview,” J. Power Sources, 161 [2] 1443–49 (2006).
2. P. Masset and R. A. Guidotti, “Thermally Activated (“Thermal”) Battery Technology Part II: Molten Salt Electrolytes,” J. Power Sources, 164 [1] 397–414 (2007).
3. P. J. Masset and R. A. Guidotti, “Thermally Activated (“Thermal”) Battery Technology Part IIIa: FeS2 Cathode Material,” J. Power Sources, 177 [2] 595–609 (2008).
4. P. J. Masset and R. A. Guidotti, “Thermally Activated (“Thermal”) Battery Technology Part IIIb: Sulfur and Oxide-based Cathode Materials,” J. Power Sources, 178 [1] 456–66 (2008).
5. R. A. Guidotti and P. J. Masset, “Thermally Activated...
("Thermal") Battery Technology Part IV: Anode Materials," *J. Power Sources*, 183 [1] 388–98 (2008).
6. S. S. Wang and R. N. Seefurth, "Electrochemical Studies of FeS₂ Electrodes in Various Sulfide-Containing Molten Salts," *J. Electrochem. Soc.*, 134 [3] 530–35 (1987).
7. S. H. Chae, S. H. Kang, H. W. Cheong, Y. S. Han, and D. H. Yoon, "Thermal Batteries with Ceramic Felt Separators – Part 1: Wetting, Loading Behavior and Chemical Stability," *Ceram. Int.*, 43 [5] 4015–22 (2017).
8. S. H. Kang, S. H. Chae, H. W. Cheong, K. H. Kim, Y. S. Han, S. M. Lee, D. H. Yoon, and J. Yi, "Thermal Batteries with Ceramic Felt Separators – Part 2: Ionic Conductivity, Electrochemical and Mechanical Properties," *Ceram. Int.*, 43 [5] 4023–28 (2017).
9. Y. Choi, H. R. Yu, and H. W. Cheong, "Electrochemical Properties of a Lithium-Impregnated Metal Foam Anode for Thermal Batteries," *J. Power Sources*, 276 102–4 (2015).
10. Y. Choi, S. Cho, and Y. S. Lee, "Effect of the Addition of Carbon Black and Carbon Nanotube to FeS₂ Cathode on the Electrochemical Performance of Thermal Battery," *J. Ind. Eng. Chem.*, 20 [5] 3584–89 (2014).
11. J. Ko, I. Y. Kim, H. M. Jung, H. Cheong, and Y. S. Yoon, "Thin Cathode for Thermal Batteries Using a Tape Casting Process," *Ceram. Int.*, 43 [7] 5789–93 (2017).
12. I. Oh, J. Cho, K. Kim, J. Ko, H. Cheong, Y. S. Yoon, and H. M. Jung, "Polyimid (co-siloxane) as a Thermo-Stable Binder for Thin Layer Cathode of Thermal Batteries," *Energies*, 11 [11] 3154 (2018).
13. J. Ko, I. Y. Kim, H. Cheong, and Y. S. Yoon, "Organic Binder-free Cathode Using FeS₂-MWCNTs Composite for Thermal Batteries," *J. Am. Ceram. Soc.*, 100 [10] 4435–41 (2017).
14. T. Yang, L. Cai, and R. E. White, "Mathematical Modeling of the LiAl/FeS₂ High Temperature Battery System," *J. Power Sources*, 201 322–31 (2012).
15. E. L. Reinholz, S. A. Roberts, C. A. Aplett, J. B. Lechman, and P. R. Schunk, "Composition and Manufacturing Effects on Electrical Conductivity of LiFeS₂ Thermal Battery Cathode," *J. Electrochem. Soc.*, 163 [8] A1723–29 (2016).
16. J. Hu, Y. Chu, Q. Tian, J. Wang, Y. Li, Q. Wu, L. Zhao, and Y. Zhu, "Film Cathode for Thermal Batteries Using a Screen-Printing Process," *Mater. Lett.*, 215 296–99 (2018).
17. S. Xie, Y. Deng, J. Mei, Z. Yang, W. M. Lau, and H. Liu, "Facile Synthesis of CoS₂/CNTs Composite and its Utilization in Thermal Battery Fabrication," *Composites, Part B*, 93 203–9 (2016).
18. S. Xie, Y. Deng, J. Mei, Z. Yang, W. M. Lau, and H. Liu, "Carbon Coated CoS Thermale Battery Electrode Material with Enhanced Discharge Performances and Air Stability," *Electrochim. Acta*, 231 287–93 (2017).
19. T. Yu, Z. Yu, Y. Can, H. Liu, X. Liu, Y. Cui, C. Wang, and Y. Cui, "Electrochemical Performances and Air Stability of Fe-depoted CoS Cathode Materials for Thermal Batteries," *Int. J. Electrochem. Sci.*, 13 7590–97 (2018).
20. J. Hu, L. Zhao, Y. Chu, Q. Tian, J. Wang, Y. Li, Q. Wu, and Y. Zhu, "Preparation and Electrochemical Properties of a New Fe₃₀Co₃₀S₃₀ Cathode Material for Thermal Batteries," *J. Alloys Compd.*, 762 109–114 (2018).
21. Y. Xie, Z. Liu, H. Ning, H. Huang, and L. Chen, "Supressing Self-Discharge of Li-B/CoS₂ Thermal Batteries by Using a Carbon-Coated CoS₂ Cathode," *RSC Adv.*, 8 [13] 7173–78 (2018).
22. C. Jin, L. Zhou, L. Fu, J. Zhu, D. Li, and W. Yang, "The Acceleration Intermediate Phase (NiS and NiS₂) Evolution by Nanocrystallization in LiNiS₂ Thermal Batteries with High Specific Capacity," *J. Power Sources*, 352 83–9 (2017).
23. C. Jin, L. Fu, J. Zhu, W. Yang, D. Li, and L. Zhou, "A Hierarchical Carbon Modified Nano-NiSₓ Cathode with High Thermal Stability for a High Energy Thermal Battery," *J. Mater. Chem. A*, 6 [16] 7123–32 (2018).
24. J. L. Payne, J. D. Percival, K. Giagloglou, C. J. Crouch, G. M. Carins, R. I. Smith, R. Comrie, R. K. B. Gover, and J. T. S. Irvine, "In-situ Thermal Battery Discharge Using NiSₓ as a Cathode Material," *ChemElectroChem*, 4 [8] 1–9 (2017).
25. C. Jin, L. Zhou, L. Fu, J. Zhu, and D. Li, "Synthesis and Discharge Performances of NiClₓ by Surface Modification of Carbon Coating as Cathode Material of Thermal Battery," *Appl. Surf. Sci.*, 402 208–13 (2017).
26. J. Hu, Y. Chu, Q. Tian, S. Guo, M. Yang, X. Wang, L. Zhao, and Y. Zhu, "Electrochemical Properties of the NiClₓ Cathode with Nickel Foam Substrate for Thermal Batteries," *Mater. Lett.*, 207 198–201 (2017).
27. W. Liu, H. Liu, S. Bi, L. Cao, and Y. Sun, "Variable-Temperature Preparation and Performance of NiClₓ as a Cathode Material for Thermal Batteries," *Sci. China Mater.*, 60 [3] 251–57 (2017).
28. K. Giagloglou, J. L. Payne, C. Crouch, R. K. B. Gover, P. A. Connor, and J. T. S. Irvine, "Transition Metal Chlorides NiClₓ, KNiClₓ, LiₓVClₓ, and LiₓMnClₓ as Alternative Cathode Materials in Primary Li Thermal Batteries," *J. Electrochem. Soc.*, 165 [14] A3510–16 (2018).
29. T. Hillel and Y. Ein-Eli, "Copper Vanadate as Promising High Voltage Cathodes for Li Thermal Batteries," *J. Power Sources*, 229 112–16 (2013).
30. J. Dai, M. Lai, R. LaFollette, and D. Reisner, "Thin Film Copper Vanadium Oxide Electrodes for Thermal Batteries," *ECS Trans.*, 33 [27] 3–9 (2011).
31. K. Giagloglou, J. L. Payne, C. Crouch, R. K. B. Gover, P. A. Connor, and J. T. S. Irvine, "Zirconium Triulfide as a Promising Cathode Material for Li Primary Thermal Batteries," *J. Electrochem. Soc.*, 163 [14] A3126–30 (2016).
32. K. Giagloglou, J. L. Payne, C. Crouch, R. K. B. Gover, P. A. Connor, and J. T. S. Irvine, "Synthesis and Electrochemical Study of CoₓNi₃ₓS₇ as a Novel Cathode Material in a Primary Li Thermal Battery," *J. Electrochem. Soc.*, 164 [9] A2159–63 (2017).
33. X. Zheng, Y. Zhu, Y. Sun, and Q. Jiao, "Hydrothermal Synthesis of MnSₓ with Different Morphology and its Performance in Thermal Battery," *J. Power Sources*, 395 318–27 (2018).
34. K. Hasegawa and S. Noda, “Lithium Ion Batteries Made of Electrodes with 99 wt% Active Materials and 1 wt% Carbon Nanotubes without Binder or Metal Foils,” *J. Power Sources*, 321 155–62 (2016).
Park, S. S. Yoon, and J. H. Ahn, “Additive-free Electrode Fabrication with Reduced Graphene Oxide Using Supersonic Kinetic Spray for Flexible Lithium-Ion Batteries,” *Carbon*, **139** 195–204 (2018).

64. B. Joshi, E. Samuel, T. G. Kim, C. W. Park, Y. I. Kim, M. T. Swhart, W. Y. Yoon, and S. S. Yoon, “Supersonically Spray-Coated Zinc Ferrite/Graphitic-Carbon Nitride Composite as a Stable High-Capacity Anode Material for Lithium-Ion Batteries,” *J. Alloys Compd.*, **765** 525–34 (2018).

65. H. Shi, S. Niu, W. Lv, G. Zhou, C. Zhang, Z. Sun, F. Li, F. Kang, and Q. H. Yang, “Easy Fabrication of Flexible and Multilayer Nanocarbon-based Cathodes with a High Unreal Sulfur Loading by Electrostatic Spraying for Lithium-Sulfur Batteries,” *Carbon*, **138** 18–25 (2018).

66. C. Y. Jung, T. S. Zhao, L. An, L. Zeng, and Z. H. Wei, “Screen Printed Cathode for Non-Aqueous Lithium-Oxygen Batteries,” *J. Power Sources*, **297** 174–80 (2015).

67. R. E. Sousa, J. Oliveira, A. Goren, D. Miranda, M. M. Silva, L. Hilliou, C. M. Costa, and S. Lanceros-Mendez, “High Performance Screen Printable Lithium-Ion Battery Cathode Ink based on C-LiFePO₃,” *Electrochim. Acta*, **196** 92–100 (2016).

68. A. Goren, J. Mendes, H. M. Rodrigues, R. E. Sousa, J. Oliveira, L. Hilliou, C. M. Costa, M. M. Silva, and S. Lanceros-Mendez, “High Performance Screen-Printed Electrodes Prepared by a Green Solvent Approach for Lithium-Ion Batteries,” *J. Power Sources*, **334** 65–77 (2016).

69. K. Y. Kang, Y. G. Lee, D. O. Shin, J. C. Kim, and K. M. Kim, “Performance Improvements of Pouch-Type Flexible Thin-Film Lithium-Ion Batteries by Modifying Sequential Screen Printing Process,” *Electrochim. Acta*, **138** 294–301 (2014).

70. Z. Tehrani, T. Korochkina, S. Govindarajan, D. J. Thomas, J. O’Mahony, J. Kettle, T. C. Claypole, and D. T. Gethin, “Ultra-Thin Flexible Screen Printable Lithium-Ion Battery,” *Graphene Mater. Res. Bull.*, **9** 2659–64 (2014).

71. W. Wang, S. Chen, J. Li, and W. Wang, “Fabrication of Catalyst Coated Membrane with Screen Printing Method in a Proton Exchange Membrane Fuel Cell,” *Int. J. Hydrogen Energy*, **40** [13] 4649–58 (2015).

72. E. F. Mine, Y. Ito, Y. Teranishi, M. Sato, and T. Shimizu, “Surface Coating and Texturing on Stainless-Steel Plates to Decrease the Contact Resistance by Using Screen Printing,” *Int. J. Hydrogen Energy*, **42** [31] 20224–9 (2017).

73. D. H. Lee, J. S. Choi, H. Chae, C. H. Chung, and S. M. Cho, “Highly Efficient Phosphorescent Polymer OLEDs Fabricated by Screen Printing,” *Displays*, **29** [5] 436–39 (2008).

74. S. Ohta, S. Komagata, J. Seki, T. Saeki, S. Morishita, and T. Asaoka, “All-Solid-State Lithium Ion Battery Using Garnet-Type Oxide and LiBO₂, Solid Electrolytes Fabricated by Screen-Printing,” *J. Power Sources*, **235** 53–6 (2013).

75. T. Syrovy, T. Kazla, L. Syrova, J. Vondrak, L. Kubac, and M. Sedlarikova, “Cathode Material for Lithium Ion Accumulators Prepared by Screen Printing for Smart Textile Applications,” *J. Power Sources*, **309** 192–201 (2016).

76. M. H. Sayed, E. V. G. Robert, P. J. Dale, and L. Gutay, “Cu₂SnS₃ Based Thin Film Solar Cells from Chemical Spray Pyrolysis,” *Thin Solid Films*, **669** 436–39 (2019).

77. Z. Liang, Z. Bi, K. Gao, Y. Fu, P. Guan, X. Feng, Z. Chai, G. Xu, and X. Xu, “Interface Modification via Al₂O₃ with Retarded Charge Recombination for Mesoscopic Perovskite Solar Cells Fabricated with Spray Deposition Process in the Air,” *Appl. Surf. Sci.*, **463** 939–46 (2019).

78. K. Y. Bae, M. W. Kim, B. H. Kim, S. H. Cho, S. S. Yoon, and W. Y. Yoon, “Effect of Electrostatic Spray Deposited Nafion Coating on Non-Lithiated LiV₂O₅ Cathode in Lithium-Metal Rechargeable Batteries,” *Solid State Ionics*, **331** 66–73 (2019).

79. X. Wu, P. Li, W. Wu, and T. Guo, “Flexible Organic Light Emitting Diodes Based on Double-Layered Graphene/PEDOT:PSS Conductive Film Formed by Spray-Coating,” *Vacuum*, **101** 53–6 (2014).

80. A. Palco, A. M. Zaidi, P. Laghi, and A. Abdellah, “Spray Deposition of Polyethylenimine Thin Films for the Fabrication of Fully-Sprayed Organic Photodiodes,” *Org. Electron.*, **23** 186–92 (2015).

81. B. Aker, R. Selyanchyn, S. Fujikawa, K. Sasaki, and S. M. Lyth, “Spray-Painted Graphene Oxide Membrane Fuel Cells,” *J. Membr. Sci.*, **541** 347–57 (2017).

82. A. B. Tahar, A. Romdhane, N. Lalaoui, N. Reverdy-Bruas, A. L. Goff, M. Holzinger, S. Cosnier, D. Chaussey, and N. Belgacem, “Carbon Nanotube-based Flexible Biocathode for Enzymatic Biofuel Cells by Spray Coating,” *J. Power Sources*, **408** 1–6 (2018).

83. Q. Guo, P. Guo, J. Li, H. Yin, J. Liu, F. Xial, D. Shen, and...
N. Li, “Fe₃O₄-CNTs Nanocomposites: Inorganic Dispersant Assisted Hydrothermal Synthesis and Application in Lithium Ion Batteries,” J. Solid State Chem., 213 104–9 (2014).

91. Q. Liu, Q. Jiang, L. Jiang, J. Peng, Y. Gao, Z. Duan, and X. Lu, “Preparation of SnO@rGO/CNTs/S Composite and Application in Lithium Ion Batteries,” J. Solid State Chem., 213 104–9 (2014).

92. M. Kazazi, Z. A. Zafar, M. Delshad, J. Cervenka, and C. Chen, “TiO₂/CNT Nanocomposite as an Improved Anode Material for Aqueous Rechargeable Aluminum Batteries,” Solid State Ionics, 320 64–69 (2018).

93. M. Y. Son, J. H. Choi, and Y. C. Kang, “Electrochemical Properties of Bare Nickel Sulfide and Nickel Sulfide-Carbon Composite Prepared by One-Pot Spray Pyrolysis as Anode Materials for Lithium Secondary Batteries,” J. Power Sources, 251 480–87 (2014).

94. Y. Yamaguchi, T. Takeuchi, H. Sakaebe, H. Kageyama, H. Senoh, T. Sakai, and K. Tatsumi, “Ab Initio Simulations of Li/Pyrite-MS₂ (M=Fe, Ni) Battery Cells,” J. Electrochem. Soc., 157 [6] A630–35 (2010).

95. A. A. AbdelHamid, X. Yang, J. Yang, X. Chen, and J. Y. Ying, “Graphene-Wrapped Nickel Sulfide Nanoprisms with Improved Performance for Li-Ion Battery Anodes and Supercapacitors,” Nano Energy, 26 425–37 (2016).

96. T. Takeuchi, H. Sakaebe, H. Kageyama, T. Sakai, and K. Tatsumi, “Preparation of NiS₂ Using Spark-Plasma-Sintering Process and its Electrochemical Properties,” J. Electrochem. Soc., 155 [9] A679–84 (2008).

97. S. W. Oh, S. T. Myung, S. M. Oh, K. H. Oh, K. Amine, B. Scrosati, and Y. K. Sun, “Double Carbon Coating of LiFePO₄ as High Rate Electrode for Rechargeable Lithium Batteries,” Adv. Mater., 22 [43] 4842–45 (2010).

98. X. Zhang, X. Zhang, X. G. Wang, Z. Xie, and Z. Zhou, “NiFe₂O₄-CNT Composite: An Efficient Electrocatalyst for Oxygen Evolution Reactions in Li-O₂ Batteries Guided by Computations,” J. Mater. Chem. A, 4 [24] 9390–93 (2016).

99. J. Yang, Y. Ouyang, H. Zhang, H. Xu, Y. Zhang, and Y. Wang, “Novel Fe₃P/Graphitized Carbon Yolk/Shell Octahedral for High-Efficiency Hydrogen Production and Lithium Storage,” J. Mater. Chem. A, 4 [25] 9923–30 (2016).

100. Z. Liu, T. Lu, T. Song, X. Y. Yu, X. W. Lou, and U. Paik, “Structure-Designed Synthesis of FeS₆@C Yolk-Shell Nanocages as a High-Performance Anode for Sodium-Ion Batteries,” Energy Environ. Sci., 10 [7] 1576–80 (2017).

101. Y. Li, Y. S. Hu, M. M. Titirici, L. Chen, and X. Huang, “Hard Carbon Microtubes Made from Renewable Cotton as High-Performance Anode Material for Sodium-Ion Batteries,” Adv. Energy Mater., 6 [18] 1600659 (2016).

102. J. Shan, Y. Liu, Y. Su, P. Liu, X. Zhuang, D. Wu, F. Zhang, and X. Feng, “Graphene-Directed Two-Dimensional Porous Carbon Frameworks for High-Performance Lithium-Sulfur Battery Cathodes,” J. Mater. Chem. A, 4 [1] 314–20 (2016).

103. Y. Sakurai, H. Ohtsuka, and J. Yamaki, “Rechargeable Copper Vanadate Cathode for Lithium Cell,” J. Electrochem. Soc., 135 [1] 32–6 (1988).

104. M. Eguchi, A. Komamura, T. Miuru, and T. Kishi, “Lithiation Characteristics of Cu₅V₂O₁₀,” J. Electrochem. Acta, 41 [6] 857–61 (1996).

105. F. Gao, J. Shi, H. Liu, S. Qiang, L. Gao, S. Bi, and W. Liu, “A Novel and Safety Lithium Thermal Battery Electrolyte – Li₇La₃ZrO₁₂ Prepared by Solid State Method,” Solid State Ionics, 326 131–35 (2018).