

Effect of CaF_2 on Phase Separation During Aluminothermic SHS Processing of Spent Lithium Ion Battery Cathode Materials

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ABSTRACT

This study investigates the role of CaF_2 in controlling phase separation during aluminothermic self propagating high temperature synthesis (SHS) of cathode material recovered from spent lithium ion batteries. The novelty of this work lies in evaluating the effect of CaF_2 content on the formation and separation of metallic and slag phases and in identifying the optimal flux concentration for processing multicomponent cathode materials. The feedstock contained Ni, Co, Mn, and Li compounds. Aluminum was used as a reducing agent, while CaF_2 was added as a flux at concentrations of 5, 10, 15, and 20 wt.%. After SHS, the products were separated into metallic and slag fractions and characterized by X ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS). The addition of CaF_2 promoted metallic phase formation and separation and contributed to the formation of an aluminate slag matrix. The metallic phase yield increased from 22.36% at 5 wt.% CaF_2 to 30.10% and 30.26% at 10 and 15 wt.%, respectively. A further increase to 20 wt.% CaF_2 reduced the metallic phase yield to 27.39%. XRD showed that LiAlO_2 was the dominant phase in the slag, while SEM/EDS confirmed the formation of a metallic phase rich in Ni with smaller amounts of Co and Al. Overall, 10 to 15 wt.% CaF_2 provided the most favorable conditions for phase separation under the studied SHS conditions.

1. Introduction

The increasing use of lithium-ion batteries has resulted in a continuous growth in the volume of spent batteries requiring recycling. However, the current recycling rate remains substantially lower than the volume of battery production and consumption. Spent lithium-ion batteries contain valuable elements, including cobalt, nickel, copper, aluminum, and lithium, which gives them considerable resource and industrial value [1]. From a circular economy perspective, recycling spent lithium-ion batteries can reduce environmental impacts, decrease the demand for primary raw materials, and return valuable components to the production cycle [2]. In particular, black mass represents an important secondary

resource because it contains lithium, cobalt, nickel, manganese, copper, and other valuable constituents. Therefore, the recovery of these metals is one of the major objectives of spent lithium-ion battery recycling [3]. Various approaches to recycling spent lithium-ion batteries have been reported, including mechanical pretreatment, hydrometallurgical leaching, pyrometallurgical reduction, closed-loop recycling, and direct regeneration of cathode materials [4-7]. Mechanical pretreatment combined with hydrometallurgical leaching in HCl media enables the recovery of valuable metals, including lithium, from lithium-ion battery waste [4]. Pyrometallurgical recycling involves high-temperature treatment and reduction processes that promote the formation of a metallic phase containing valuable battery compo-

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nents. During thermal processing, cathode materials undergo decomposition, while nickel, cobalt, and manganese can be transferred to a metallic or alloy phase. One advantage of this approach is the possibility of concentrating valuable metals in a metallic phase with relatively limited pretreatment of the feed material [5]. Closed-loop recycling aims to separate the components of spent lithium-ion batteries and return valuable materials to the production cycle. The recovered feedstock can subsequently be used for the resynthesis of cathode materials, thereby reducing the demand for primary resources [6]. Direct regeneration, in contrast, is intended to restore the original composition, structure, and electrochemical properties of degraded cathode materials. Hydrothermal relithiation is one approach that can replenish lithium lost from the cathode structure and restore its electrochemical activity. The principal advantage of direct regeneration is the possibility of reusing cathode materials without completely decomposing them into individual components [7]. The choice of a recycling route therefore depends on the required degree of metal recovery, the process temperature, and whether preservation of the cathode structure is necessary. Among high-temperature treatment methods, SHS is of particular interest. SHS is based on an exothermic reaction that, after local initiation, propagates through the reaction mixture using the heat released by the reaction itself. The applicability of SHS to lithium-ion battery recycling has been demonstrated for black mass containing lithium, nickel, cobalt, and manganese in complex oxide compounds [8]. Aluminothermic reduction of lithium cobalt oxide has also demonstrated the possibility of recovering cobalt as a metallic or Co, Al alloy phase while transferring lithium to the slag phase [9]. Aluminothermic reduction has similarly been investigated for manganese-containing oxide systems [10]. In nickel-containing systems, aluminothermic reduction of nickel oxide can lead to the formation of Ni, Al intermetallic phases. The synthesis of nickel aluminides from oxide raw materials by aluminothermic processing further demonstrates the applicability of this approach to oxide materials containing nickel and other transition metals [11]. These findings indicate that aluminothermic SHS is a promising approach for processing spent lithium-ion battery cathode materials containing Ni, Co, Mn, and Li compounds. Phase separation during aluminothermic processing is strongly influenced by the properties of the slag phase. In CaO, SiO₂, Al₂O₃ slag systems, increasing the CaF₂ content from 3 to 11 wt.% has been reported to decrease the melt viscosity at

1300 °C from 0.854 to 0.241 Pa·s, thereby improving slag fluidity [12]. Similarly, in CaF₂, CaO, Al₂O₃, MgO, TiO₂ slag systems, increasing the CaF₂ content decreases melt viscosity and viscous-flow activation energy through structural modification of the melt [13]. During reduction smelting of lithium-ion battery cathode materials, fluoride-containing additives have also been reported to promote the transfer of Co, Ni, and Mn into a metallic alloy phase, while lithium is concentrated mainly in the dust fraction as Li₂CO₃ and LiF [14]. Considering the influence of lithium-containing components on the properties of aluminate slags as well as the possible evaporation of fluoride species, CaF₂ content was selected as the key experimental parameter in the present study. Variation of the CaF₂ content provides a means of controlling slag formation and the separation between metallic and slag phases [15]. Recent studies have reported further advances in the recycling of spent lithium ion batteries, including improvements in pyrometallurgical processing, cathode material recycling, and integrated recycling strategies [16–20]. Recent developments in pyrometallurgical treatment have focused on improving metal recovery and process efficiency through optimized thermal processing routes [16, 17]. These studies demonstrate the continuing development of recycling technologies and support further investigation of alternative thermal approaches for the recovery of valuable metals from spent battery materials [18–20]. This study aimed to determine the effect of CaF₂ content on phase separation during aluminothermic SHS processing of spent lithium ion battery cathode material and to identify the optimal CaF₂ range based on metallic-phase yield and slag phase composition.

2. Experimental Section

2.1. Taring Materials and Isolation of Cathode Material

Cylindrical 18650 lithium ion batteries from an end of life electric scooter battery pack were used as the starting material. Before disassembly, the residual charge was neutralized. The cells were opened under controlled laboratory conditions and separated into the copper anode current collector, separator, aluminum cathode current collector, and active cathode layer. The cathode material contained lithium and transition metal oxides, conductive carbon, and residual binder. It was separated from the aluminum foil by ultrasonic treatment followed by mechanical scraping of the remaining material. The

recovered cathode material was dried at 80 °C for 48 h to remove residual moisture and volatile components. The dried material was ground in an agate mortar to obtain a homogeneous powder and ensure uniformity during preparation of the reaction mixtures. For consistency, the recovered and homogenized cathode powder is referred to as cathode material throughout the manuscript. After SHS, the separated products are referred to as the metallic phase and slag phase.

2.2. Initial Cathode Material Composition

The elemental composition of the initial cathode material was determined by X ray fluorescence spectroscopy (XRF) using a Thermo Scientific ARL Perform'X spectrometer. Before analysis, the cathode material was dried at 80 °C for 48 h and homogenized in an agate mortar. The powder was pressed into a 30 mm diameter pellet under a load of 20 t. The instrument was calibrated using certified reference standards. Characteristic K α and L α spectral lines were acquired sequentially. The detection limit was approximately 0.01 wt.%. The material contained Li, Ni, Co, Mn, Al, Cu, and C. Ni, Co, and Mn originated mainly from the cathode active material, while Al and Cu were associated with the current collectors. The high carbon content was attributed to conductive carbon and residual electrode components. The quantitative composition is presented in Table 1. The morphology and local elemental composition of the initial cathode material were also examined by SEM/EDS. SEM analysis was performed using a Thermo Fisher Quattro S microscope equipped with an Anax 60PM B EDS system. SEM was used to examine the cathode powder morphology, while EDS was used to confirm the presence of the principal elements. A separate XRD analysis of the initial cathode material was not performed. XRD was later applied to the slag products as described in Section 2.5.

Unquantified fraction was calculated by difference and is expected to consist mainly of oxygen and residual nonmetallic components. The identical Li and Co contents of 3.29 wt.% were verified against the original analytical data and are not typographical errors. The quantified components accounted for 74.44 wt.% of the cathode material. The remaining 25.56 wt.% was calculated by difference and represents the unquantified fraction. This fraction is expected to consist mainly of oxygen associated with oxide phases and residual nonmetallic components such as binder. The values in Table 1 were obtained from the homogenized cathode sample and are not

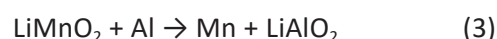
averages of replicate measurements. Therefore, statistical parameters were not calculated.

Table 1. Elemental composition of the initial cathode material

Element	Content, wt.%
Li	3.29
Co	3.29
Ni	26.60
Mn	0.38
Al	0.62
Cu	0.26
C	40.0
Unquantified fraction*	25.56
Total	100.00

2.3. Preparation of Aluminothermic Charges

PA-4 aluminum powder with a nominal particle size of $\leq 50 \mu\text{m}$ was used as the reducing agent. Information on the manufacturer and certified purity was not available in the retained material documentation. Aluminum was used to reduce oxides containing Ni, Co, and Mn. The principal reduction reactions considered in this study are given in Eqs. (1) to (3):



Equations (1) to (3) represent simplified condensed phase aluminothermic reduction pathways. Under the present conditions, metallic lithium was not considered a stable product. Lithium remained in oxidized phases, while Al reduced the transition metal components. Thermodynamic calculations by Nababan et al. [9] using FactSage 8.2 and Gibbs energy minimization showed that aluminothermic treatment of LiCoO_2 with Al favors the formation of metallic Co or a Co and Al alloy, while lithium remains mainly in Li_2O and LiAlO_2 . The reaction is highly exothermic and can provide sufficient heat for ignition and melting of the reaction mixture. This is consistent with the present XRD results, where LiAlO_2 was the dominant slag phase. The Al to cathode material mass ratio was fixed at 0.37, corresponding to 0.74 g Al per 2.00 g of cathode material, based on preliminary SHS trials. This ratio was kept constant in all experiments. CaF_2 was used as a flux to improve slag fluidity and promote sepa-

ration between the metallic and slag phases. Only the CaF_2 content was varied to evaluate its effect on phase separation. CaF_2 was added at 5, 10, 15, and 20 wt.% relative to the cathode material mass. The batch compositions are presented in Table 2.

The data in Table 2 show that the mass of the cathode material and aluminum powder remained constant across all compositions, amounting to 2.00 and 0.74 g, respectively. The CaF_2 mass was varied from 0.10 to 0.40 g, corresponding to additions of 5, 10, 15, and 20 wt.% relative to the 2.00 g cathode material.

2.4. Aluminothermic SHS Processing

Aluminothermic SHS was carried out in a flow through reactor under nitrogen. Before each experiment, the reactor was purged with nitrogen to maintain an inert atmosphere during the SHS reaction. The prepared mixture was placed on a heat resistant support in the center of the reactor and locally ignited. After ignition, the reaction became self sustaining and the combustion front propagated through the mixture. The process was recorded using an Evercam C4 1000 high speed camera at 500 fps with a resolution of 1280×800 pixels. The recorded sequence corresponded to the mixture containing 15 wt.% CaF_2 . After the reaction, the products were cooled under nitrogen and separated into metallic and slag fractions. Each fraction was dried and weighed.

The yields of the metallic and slag phases were calculated using Eqs. (4) and (5):

$$\eta_{\text{metal}} = \frac{m_{\text{metal}}}{m_{\text{charge}}} \cdot 100\% \quad (4)$$

$$\eta_{\text{slag}} = \frac{m_{\text{slag}}}{m_{\text{charge}}} \cdot 100\% \quad (5)$$

where: η_{metal} and η_{slag} – the yields of the metallic and slag phases, m_{metal} and m_{slag} – their respective masses, and m_{charge} – the total initial mass of the charge including cathode material, Al, and CaF_2 .

2.5. X-ray Diffraction Analysis

The phase composition of the slag products was determined by XRD using a Rigaku MiniFlex 600 diffractometer. The analysis was performed using $\text{Cu K}\alpha$ radiation, whose wavelength is $\lambda = 1.5406 \text{ \AA}$. Diffraction patterns were recorded in the 2θ range of 10 to 80° with a step size of 0.02° and a scanning speed of $2^\circ/\text{min}$. Prior to analysis, the slag products were separated from the metallic phase, ground in an agate mortar, and placed in a sample holder. The resulting diffraction patterns were used to identify crystalline phases in the slag formed as a result of the SHS reaction.

2.6. SEM/EDS Analysis of the Metallic Phase

The morphology and elemental composition of the metallic phase were studied using a JEOL JSM-6490LA scanning electron microscope equipped with an Oxford Instruments X-Max 80 mm^2 energy-dispersive spectroscopy spectrometer. Metal fragments were separated from the reaction products, mounted on a sample holder, and analyzed at an accelerating voltage of 20 kV and a probe current of 1 nA. SEM images were used to evaluate the surface morphology of the metallic phase and the features of the metal slag interface. EDS analysis was performed at several points on the sample surface to determine the amounts of Ni, Co, Al, Mn, O, and Ca. The results were used to assess the degree of reduction of transition metals and confirm the formation of a metallic phase based on Ni, Co, and Al.

3. Results and Discussion

3.1. SHS Reaction Behavior

A high speed recording of the mixture containing 15 wt.% CaF_2 was used to observe the SHS reaction from ignition to completion. The reaction was carried out under nitrogen in a flow through reactor. The recorded frames are shown in Fig. 1.

Table 2. Composition of aluminothermic mixtures with different CaF_2 additions

CaF_2 addition, wt.% relative to cathode material	Cathode material, g	Al, g	CaF_2 , g	Total mass of the mixture, g
5	2.00	0.74	0.10	2.84
10	2.00	0.74	0.20	2.94
15	2.00	0.74	0.30	3.04
20	2.00	0.74	0.40	3.14

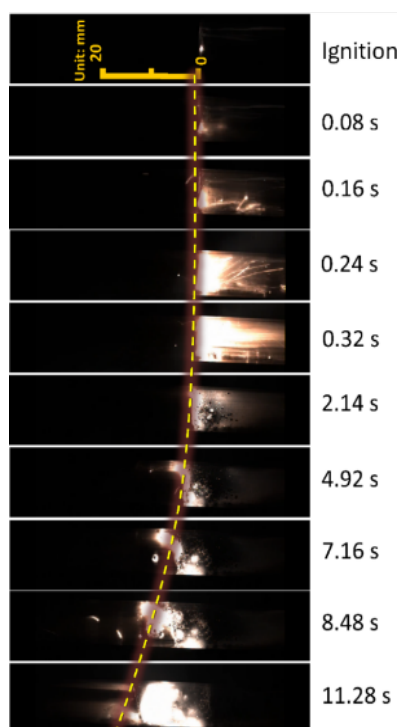


Fig. 1. Sequential frames of the SHS reaction for a mixture containing 2.00 g cathode material, 0.74 g Al, and 0.30 g CaF_2 corresponding to 15 wt.% CaF_2 relative to the cathode material.

As shown in Fig. 1, after local ignition, the reaction rapidly became self sustaining. During the initial stage, the combustion front propagated through the sample and a bright reaction zone was observed. As the reaction progressed, molten products moved toward the lower part of the reactor. At the final stage, liquid products accumulated and separated into metallic and slag phases.

3.2. Effect of CaF_2 Content on the Yields of Metallic and Slag Phases

The CaF_2 content was varied within the range of 5–20 wt.% to evaluate its effect on the separation of the products formed during the aluminothermic SHS process. After completion of the reaction, the resulting material was separated into metallic and

slag fractions. The mass of each fraction was determined, and its yield was calculated relative to the initial mass of the charge. The experimental results, including the masses and yields of the metallic and slag phases as well as the calculated mass loss, are presented in Table 3.

As shown in Table 3, increasing the CaF_2 content from 5 to 10 wt.% increased the metallic phase yield from 22.36% to 30.10%. A further increase to 15 wt.% resulted in a similar yield of 30.26%. At 20 wt.% CaF_2 , the metallic phase yield decreased to 27.39%, while the slag yield increased to 57.17%. These results indicate that 10 to 15 wt.% CaF_2 provides the most favorable range for phase separation.

The observed effect is attributed to the fluxing action of CaF_2 . Previous studies have shown that CaF_2 can reduce slag viscosity and improve melt fluidity [12, 13]. Under the present conditions, improved fluidity may promote the movement and coalescence of metallic droplets and facilitate their separation from the slag. The decrease in metallic yield at 20 wt.% CaF_2 indicates that further addition does not improve metal recovery. Similar preferential transfer of Co, Ni, and Mn into a metallic alloy phase has been reported during reduction smelting of spent lithium ion battery materials [14].

3.3. Phase Composition of Slag Products According to XRD Data

The slag products obtained with 5, 10, 15, and 20 wt.% CaF_2 were analyzed by XRD. The corresponding patterns are shown in Fig. 2. LiAlO_2 was the dominant phase in all samples. Weaker reflections from secondary phases containing Ni, Mn, and Al varied with CaF_2 content. The identified phases and their contents are summarized in Table 4.

LiAlO_2 was the dominant crystalline phase in all slag samples, with a content of 75.0–89.9%. The $\gamma\text{-Al}_2\text{O}_3$ content decreased from 19.4% at 5 wt.% CaF_2 to 0.8% at 10 wt.% CaF_2 . Secondary Ni- and Mn-containing phases, including NiAl_2O_4 , LiMnO_4 , and Mn_2O_3 , were detected depending on the CaF_2 content, indi-

Table 3. Effect of CaF_2 content on the yield of metallic and slag phases

CaF_2 content, wt. %	Total charge mass, g	Metallic phase, g	Metallic phase yield, %	Slag, g	Slag yield, %	Mass loss, %
5	2.84	0.635	22.36	1.43	50.35	27.29
10	2.94	0.885	30.10	1.34	45.58	24.32
15	3.04	0.920	30.26	1.51	49.67	20.07
20	3.14	0.860	27.39	1.79	57.17	15.44

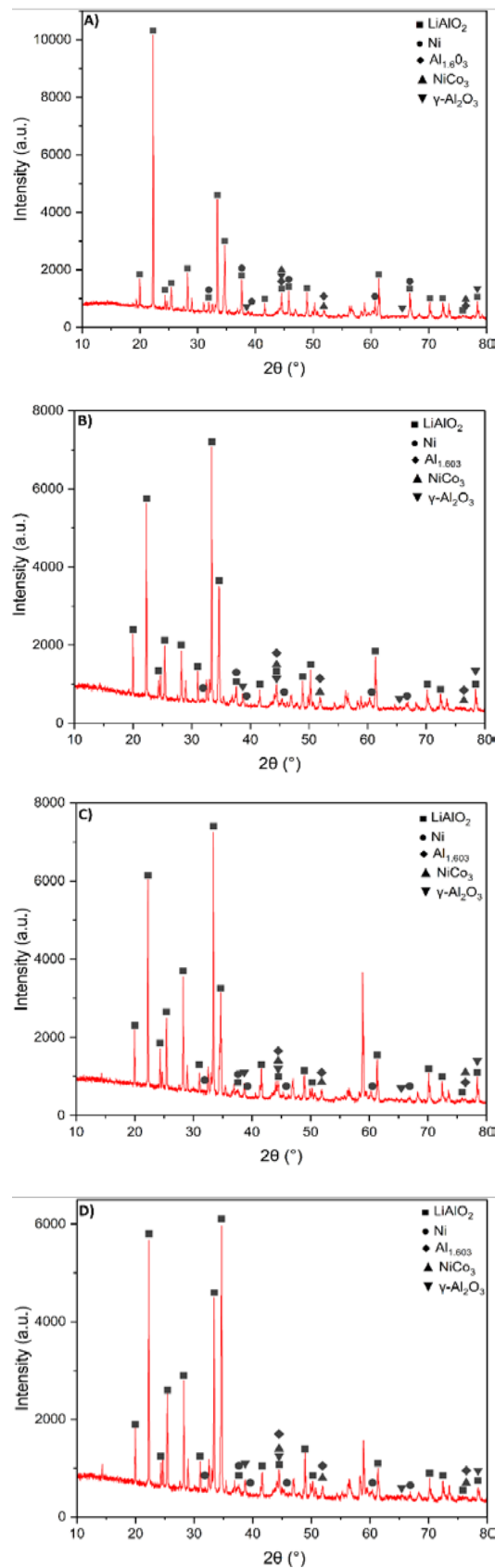


Fig. 2. XRD patterns of slag products obtained after the SHS reaction with different CaF_2 contents: (A) 5 wt.% CaF_2 , (B) 10 wt.% CaF_2 , (C) 15 wt.% CaF_2 , and (D) 20 wt.% CaF_2 . Corresponding ICDD PDF reference cards for phase identification are $\gamma\text{-LiAlO}_2$ (No. 38-1464), Ni (No. 04-0850), NiCO_3 (No. 12-0771), and $\gamma\text{-Al}_2\text{O}_3$ (No. 10-0425).

cating partial retention of transition-metal-containing species in the slag. These phase changes are consistent with the fluxing role of CaF_2 reported for related oxide slag systems [12,13]. Together with the metallic-phase yield data, the XRD results support 10-15 wt.% CaF_2 as the most favorable range for metal-slag separation.

3.4. Morphology and Elemental Composition of the Metallic Phase by SEM/EDS

The metallic fraction obtained after the aluminothermic SHS reaction was studied to assess the reduction of transition metals and the quality of separation of the metal-slag system. The surface morphology and the nature of the interphase

Table 4. Major phases of slag products after the SHS reaction at different CaF_2 contents

CaF_2 content, wt.%	Main identified phases	Phase content, %
5	LiAlO_2	75.0
	$\gamma\text{-Al}_2\text{O}_3$	19.4
	Ni	2.2
	NiCO_3	1.8
	$\text{Al}_{1.6}\text{O}_3$	1.6
	Co_3O_4	0.1
10	LiAlO_2	89.9
	$\gamma\text{-Al}_2\text{O}_3$	0.8
	LiMnO_4	2.0
	Mn_2O_3	0.5
	AlNi	1.8
	Co	0.2
15	CoO	1.0
	LiAlO_2	87.8
	Ni	1.7
	Co	2.1
	NiAl_2O_4	1.6
	AlNi	0.8
20	Al, Mn	0.7
	LiAlO_2	89.5
	Ni	1.7
	NiAl_2O_4	2.3
	AlNi	1.0
	LiMnO_4	2.7
	Mn_2O_3	1.2
	$\text{AlO}(\text{OH})$	0.6

boundary were studied by SEM, and the elemental composition was determined using EDS analysis. The results are shown in Fig. 3. The SEM image shows a dense metallic region with a clearly defined boundary between the metal and slag. This structure indicates the merging of molten metal droplets and the formation of an independent metallic fraction. As shown in Fig. 3(c), the metallic phase consisted predominantly of Ni (85.6 wt.%), with smaller amounts of Co (6.4 wt.%) and Al (6.0 wt.%). The high nickel content indicates the efficient reduction of nickel containing components of the cathode material, while the presence of Co is associated with its co-reduction with Ni. The detected Al can be explained by the participation of aluminum as a reducing agent, as well as the possible formation of local Ni-Al-containing areas. The predominance of Ni together with the presence of Co and Al confirms the formation of a Ni, Co, Al metallic phase rather than isolated reduced particles. The compact morphology and distinct metal-slag boundary also indicate effective coalescence of the metallic droplets and their separation from the oxide matrix.

The obtained results confirm the formation of metallic products in the Ni, Co, Al system and are con-

sistent with the slag phase composition determined by X-ray diffraction and the measured metallic phase yields. These results demonstrate that the most effective separation of the metallic and oxide phases occurs at a CaF_2 content of 10–15 wt.%.

4. Conclusion

This study investigated the effect of CaF_2 content on phase separation during aluminothermic SHS processing of spent lithium ion battery cathode material. The CaF_2 content strongly influenced the yields of the metallic and slag phases. Increasing the CaF_2 content from 5 to 10 wt.% increased the metallic phase yield from 22.36% to 30.10%. A similar value of 30.26% was obtained at 15 wt.% CaF_2 . When the CaF_2 content was increased to 20 wt.%, the metallic phase yield decreased to 27.39%, while the slag yield increased to 57.17%. XRD analysis showed that LiAlO_2 was the dominant crystalline phase in all slag samples. The $\gamma\text{-Al}_2\text{O}_3$ content decreased markedly at 10 wt.% CaF_2 , indicating more complete formation of the aluminate slag matrix. Secondary phases including NiAl_2O_4 , LiMnO_4 , and Mn_2O_3 were also detected, showing that part of the transition

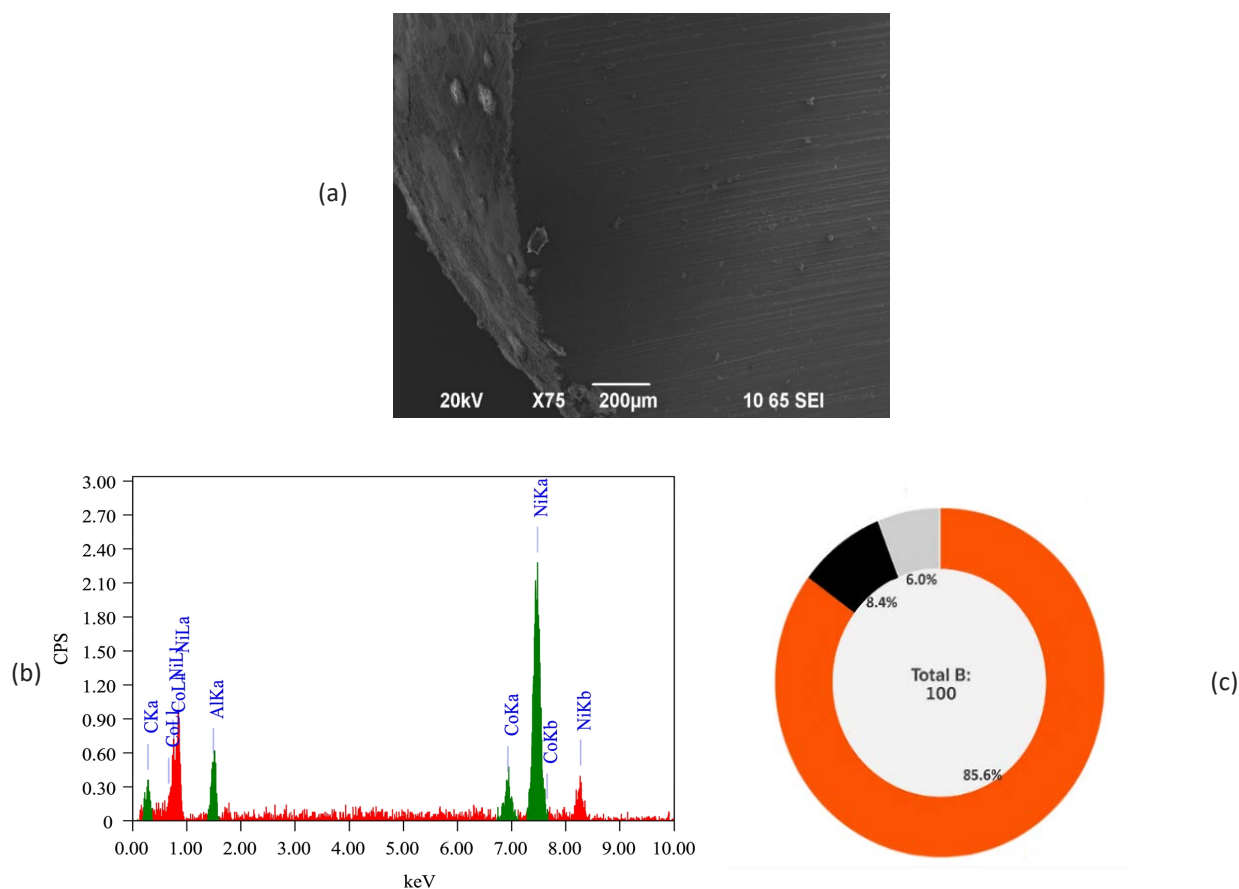


Fig. 4. SEM/EDS results for the metallic phase obtained after SHS with 15 wt.% CaF_2 . (a) SEM image. (b) EDS spectrum. (c) Elemental composition in wt.%.

metals remained in the oxide phase. SEM/EDS confirmed the formation of a dense metallic fraction containing mainly Ni, with smaller amounts of Co and Al. The combined yield, XRD, and SEM/EDS results indicate that 10 to 15 wt.% CaF_2 provides the most favorable conditions for phase separation under the studied SHS conditions. In this range, the metallic phase yield reached its highest values and separation between the metallic and slag products was most effective. Further increase in CaF_2 content did not improve the metallic phase yield.

Author Contributions

Shyngyskhan Sultakhan – Investigation, Methodology, Data Curation, Formal Analysis, Visualization, Writing – Original Draft, Writing – Review & Editing. **Tair Makhsutov** – Conceptualization, Methodology, Investigation, Data Curation, Formal Analysis, Validation, Visualization, Resources, Software, Writing – Original Draft, Writing – Review & Editing. **Meiram Atamanov** – Conceptualization, Methodology, Investigation, Formal Analysis, Supervision, Resources, Validation, Writing – Original Draft, Writing – Review & Editing. **Kairgaly Zhumadil** – Investigation, Data Curation, Formal Analysis, Visualization, Validation, Writing – Original Draft, Writing – Review & Editing. **Seilbek Malik** – Investigation, Data Curation, Formal Analysis, Validation, Writing – Review & Editing. **Tatyana Kan** – Investigation, Methodology, Data Curation, Formal Analysis, Validation, Writing – Original Draft, Writing – Review & Editing. **Viatcheslav Bykov** – Conceptualization, Methodology, Investigation, Formal Analysis, Resources, Validation, Supervision, Writing – Original Draft, Writing – Review & Editing. **Fyodor Malchik** – Conceptualization, Methodology, Investigation, Formal Analysis, Supervision, Resources, Validation, Writing – Original Draft, Writing – Review & Editing.

Conflict of Interest

The authors declare that they have no conflict of interest.

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Влияние CaF_2 на фазовое разделение при алюмотермической CBC-переработке катодных материалов отработанных литий-ионных батарей

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АННОТАЦИЯ

В данном исследовании изучена роль CaF_2 в регулировании фазового разделения при алюмотермическом самораспространяющемся высокотемпературном синтезе (CBC) катодного материала, выделенного из отработанных литий-ионных батарей. Новизна работы заключается в оценке влияния содержания CaF_2 на формирование и разделение металлической и шлаковой фаз, а также в определении оптимальной концентрации флюса для переработки многокомпонентных катодных материалов. Исходный материал содержал соединения Ni, Co, Mn и Li. В качестве восстановителя использовали алюминий, а CaF_2 добавляли в качестве флюса в количестве 5, 10, 15 и 20 мас.%. После CBC продукты разделяли на металлическую и шлаковую фракции и исследовали методом рентгеновской дифракции (XRD) и сканирующей электронной микроскопии с энергодисперсионной спектроскопией (SEM/EDS). Добавление CaF_2 способствовало формированию и разделению металлической фазы и образованию алюминатной шлаковой матрицы. Выход металлической фазы увеличился с 22.36% при 5 мас.% CaF_2 до 30.10% и 30.26% при 10 и 15 мас.%, соответственно. Дальнейшее увеличение содержания CaF_2 до 20 мас.% снизило выход металлической фазы до 27.39%. По данным XRD основной фазой шлака являлся LiAlO_2 , а SEM/EDS подтвердил образование металлической фазы с преобладанием Ni и меньшим содержанием Co и Al. В целом содержание CaF_2 в диапазоне 10-15 мас.% обеспечило наиболее благоприятные условия для фазового разделения в исследованных условиях CBC.

Ключевые слова: отработанные литий ионные батареи, алюмотермический CBC, фторид кальция, фазовое разделение, извлечение металлов

Пайдаланылған литий ионды батареялардың катодтық материалдарын алюмотермиялық ӨТЖС өңдеу кезінде CaF_2 әсерінен фазалық бөліну

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АҢДАТПА

Бұл зерттеуде пайдаланылған литий ионды батареялардан алынған катодтық материалдарды алюмотермиялық өздігінен таралатын жоғары температуралы синтез (ӨТЖС) әдісімен өңдеу кезінде CaF_2 фазалық бөлінуді реттеудегі рөлі зерттелді. Жұмыстың жаңалығы CaF_2 мөлшерінің металдық және қож фазаларының түзілуі мен бөлінуіне әсерін бағалауда және көпкомпонентті катодтық материалдарды өңдеу үшін флюстің оңтайлы мөлшерін анықтауда жатыр. Бастапқы материал құрамында Ni, Co, Mn және Li қосылыстары болды. Тотықсыздандырғыш ретінде алюминий қолданылды, ал CaF_2 5, 10, 15 және 20 мас.% мөлшерінде флюс ретінде қосылды. ӨТЖС аяқталғаннан кейін өнімдер металдық және қождық фракцияларға бөлініп, рентгендік дифракция (XRD) және энергия дисперсиялық спектроскопиямен жабдықталған сканерлеуші электрондық микроскопия (SEM/EDS) әдістерімен зерттелді. CaF_2 қосу металдық фазаның түзілуі мен бөлінуіне ықпал етіп, алюминатты қож матрицасының қалыптасуына әсер етті. Металдық фазаның шығымы 5 мас.% CaF_2 кезінде 22.36%-дан 10 және 15 мас.% кезінде тиісінше 30.10% және 30.26%-ға дейін артты. CaF_2 мөлшерін 20 мас.% дейін одан әрі арттыру металдық фазаның шығымын 27.39%-ға дейін төмендетті. XRD нәтижелері қождағы негізгі фазаның LiAlO_2 екенін көрсетті, ал SEM/EDS құрамында негізінен Ni және аз мөлшерде Co мен Al болатын металдық фазаның түзілгенін растады. Жалпы алғанда, 10-15 мас.% CaF_2 зерттелген ӨТЖС жағдайларында фазалық бөліну үшін ең қолайлы жағдайларды қамтамасыз етті.

Түйін сөздер: пайдаланылған литий ионды батареялар, алюмотермиялық SHS, кальций фториді, фазалық бөліну, металдарды қалпына келтіру