

Innovative Approaches to Lithium Recycle and Reuse of Chemical Strengthening Salt in Display Cover Glass Manufacturing

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Abstract

This study presents a circular usage system for lithium in the glass manufacturing process by recovering it through chemical crystallization (CC). A thermodynamic simulation has identified sulfate as an effective additive. The process enhanced glass strength by separating lithium from the chemical strengthening salt, proving its applicability in sustainable manufacturing.

Author Keywords

cover glass; chemical strengthening; lithium recycling; sustainable process

1. Introduction

Electronic devices are essential to daily life. Accordingly, the demand for lithium, as a critical component of batteries and display cover glasses, is constantly increasing. However, lithium resources are limited and a recycling system is required to ensure its efficient use [1, 2]. Thus, a life-cycle approach that recovers lithium from products and reintegrates it into new products is proposed. This study focuses on a method for recovering lithium released from a glass substrate during the chemical strengthening process, which is a part of display cover glass manufacturing.

Lithium aluminosilicate glass is widely used because of the growing demand for high-strength cover glasses. In the chemical strengthening process, compressive stress is applied near the surface by ion-exchanging lithium ions in the glass with sodium ions in molten nitrate, resulting in high strength [3]. However, repeated strengthening led to the accumulation of lithium in nitrate and a consequent decrease in compressive stress. In conventional processes, the deteriorated nitrate is discarded, causing a reduction in lithium resources. Therefore, a process to separate lithium from used nitrate is essential for realizing sustainable lithium usage.

Conventional methods for separating and recovering lithium, including solvent extraction [4] and generating lithium carbonate by adding carbonate to aqueous solution [5], have been studied. However, these methods involve water and require new separation equipment adjacent to the chemical strengthening process that manages the molten nitrate. Regarding molten salt handling, two methods are available for separating impurity ions, such as sodium or lithium, in chemical strengthening molten salt. The first involves the absorption of alkali ions using ion sieves [6]. Although absorption properties can be designed by controlling the particle size and specific surface area, there is a concern that the absorbent may adhere to the glass surface and cause appearance issues in strengthened glass. The second method involves the generation of metal components with impurities by the addition of anions [7]. The deposited solids are separated by sedimentation or filtering, which require large-scale equipment. Therefore, a method based on CC (chemical crystallization) involves the precipitation of crystals, including target alkali metals, through the addition of an appropriate anion to molten nitrate and proper cooling and collection of the precipitate [8]. This method is expected to restore molten nitrate and recover lithium without significant investments. This report

demonstrates the verification of the CC process as a lithium recovery method in nitrate used for chemical strengthening and its applicability to mass manufacturing processes.

2. Experiment

(1) Thermodynamic simulation

A thermodynamic equilibrium simulation was conducted for a mixture of 45 g KNO_3 , 45 g NaNO_3 , and 10 g LiNO_3 with the addition of 15% NaCl , NaOH , Na_2SO_4 , and Na_2CO_3 , respectively. The process was thermodynamically simulated using FactSage (ver. 8.2) [9].

(2) Li recovery test

An SUS304 stainless-steel pot was prepared, and a mixture of 60.0 wt.% KNO_3 , 40.0 wt.% NaNO_3 , and 10.0 wt.% LiNO_3 was heated to over 400°C to prepare molten salt. Subsequently, 25.0 wt.% Na_2SO_4 was added and completely dissolved. As shown in Figure 1, a recovery jig made of an SUS304 stainless-steel metal mesh plate was prepared. Figure 2 illustrates a schematic flow of the CC process. The jig was immersed in the molten salt, which was then cooled to approximately 300 °C. After a few hours of immersion, the jig was removed, and the solids adhering to the metal mesh were partially collected. The jig was immersed in water to collect the solids as a water solution. Subsequently, sulfate and nitrate, which do not contain lithium, were added to refill the molten salt weight according to the amount of collected solids. The molten salt was then reheated to over 400 °C until it was fully dissolved.

(3) Chemical strengthening test

A 0.7 mm thick substrate of Dragontrail™ STAR2 (AGC Inc., Japan), a lithium aluminosilicate glass, was prepared and ion-exchanged at 410 °C for 2 h in the molten salt before and after the CC process.

(4) Characterization

The lithium concentrations in the molten salt and collected solids were measured using an atomic absorption spectrophotometer ZA3300 (Hitachi High-Technologies, Japan). The crystal structures of the collected solids were analyzed using an X-ray diffractometer (SmartLab, Rigaku Co., Japan). The ion-exchanged glass was visually inspected, and the residual stress was measured using a scattered light polariscope SLP-2000 (Orihara Seisakusho, Japan). Drop strength was estimated in accordance with the procedure proposed in the previous study using the compressive stress [3].

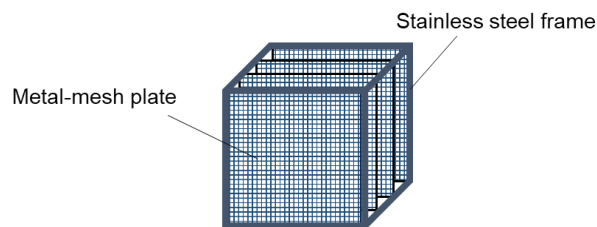


Figure 1. Schematic of the recovery jig

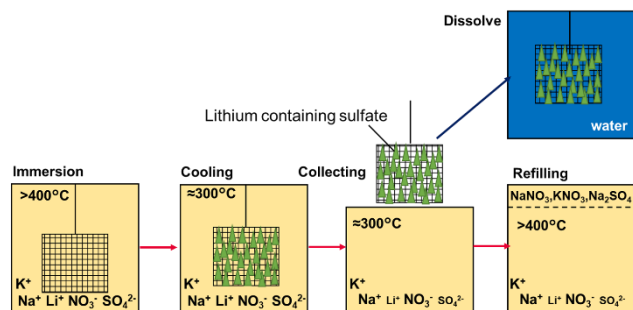


Figure 2. Chemical crystallization flow

3. Results

(1) Thermodynamic simulation

The weight ratio of solids produced in the molten salt containing NaCl, NaOH, Na₂SO₄, and Na₂CO₃ was predicted by thermodynamic equilibrium simulation at temperatures between 200 and 500 °C. Case studies involving the addition of sulfate and carbonate are shown in Figure 3 and Figure 4, respectively. Among the anion species examined, NaLiSO₄ precipitated with the addition of sulfate, and its weight increased as the temperature decreased. No lithium-containing solids were generated with chloride or hydroxide, whereas Li₂CO₃ precipitated with carbonate. However, carbonates are expected to cause haze on glass surfaces because of the alkalinization of the molten salt [10]. Based on these data, sulfate was selected as a suitable candidate additive anion when salts were used for chemical strengthening.

(2) Li recovery test

Figure 5 shows the appearance of the recovery jig after its removal from the molten salt. The metal mesh plates of the jig are nearly completely covered with a white solid. Figure 6 shows an optical image of the solids collected from the recovery jig. The solids appear to be a mixture of needle-shaped crystals and other white solids. They are easily dissolved in water.

The weight ratios and lithium concentrations of the molten salt and collected solids are listed in Table 1. The Li concentration in the collected solids was approximately three times higher than that in the molten salt before the CC process. In addition, the Li concentration in the molten salt was reduced by approximately 23% via the CC process.

The corresponding X-ray diffraction patterns are shown in Figure 7. Li₂NaK(SO₄)₂ was identified as a Li-containing material. In addition, NaNO₃, KNO₃, Na₂SO₄ and Na₃(NO₃)(SO₄)·H₂O were identified.

(3) Characteristics of chemical strengthened glass

The strengthened glass substrate samples exhibited no visible surface defects before or after the CC process. Figure 8 shows the drop strength of the strengthened glass calculated from the measured stress of the strengthened samples before and after the CC process [3]. The strength of the glass strengthened by the molten salt after the CC process improved to the same level as that achieved using the initially designed molten salt despite replacing only 7.4% of the salt before the CC process. These results demonstrate that the CC process lowers the Li concentration in the deteriorated molten salt and enables its reuse for chemical strengthening during mass manufacturing.

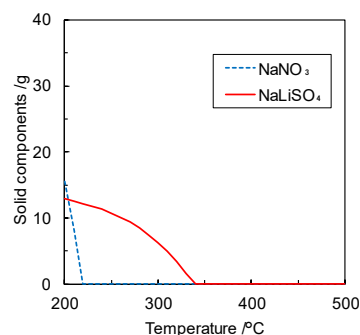


Figure 3. Weight ratio of solid components in the mixture of 45 g KNO₃, 45 g NaNO₃, and 10 g LiNO₃ with 15% Na₂SO₄ between 200 and 500 °C based on thermodynamic simulations.

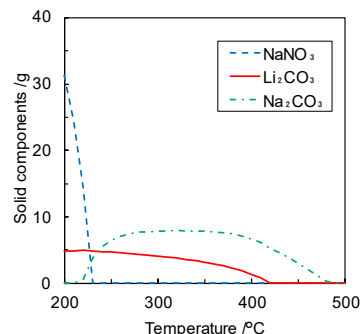


Figure 4. Weight ratio of solid components in the mixture of 45 g KNO₃, 45 g NaNO₃, and 10 g LiNO₃ with 15% Na₂CO₃ between 200 and 500 °C based on thermodynamic simulations.



Figure 5. Appearance of the recovery jig after the CC process.

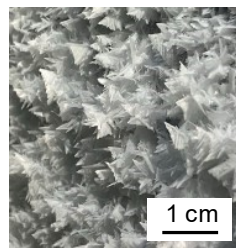
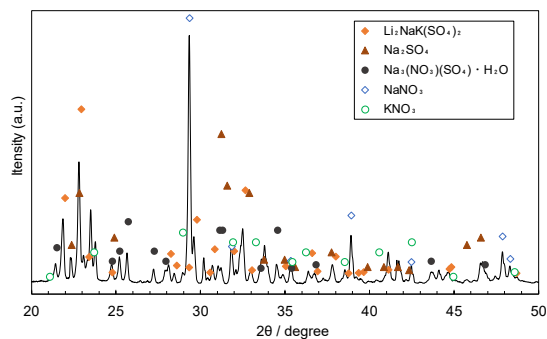
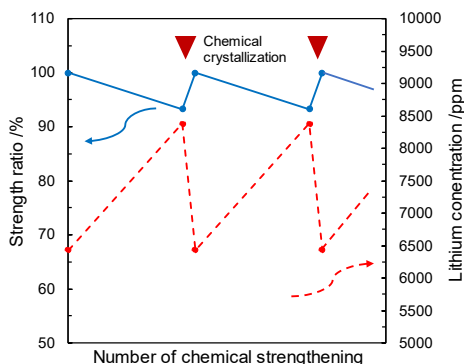


Figure 6. An optical image of the collected solids on the recovery jig.

Table 1. Weight ratio and Li concentration of molten salt and collected solids before and after CC.

		Weight ratio	Li conc. (ppm)
Before CC process		100.0%	8 380
CC	Molten salt	92.6%	6 940
	Collected solids	7.4%	25 600
After CC process		100.0%	6 430
Li ₂ NaK(SO ₄) ₂		-	51 780

**Figure 7.** X-ray diffraction pattern of the collected solids.**Figure 8.** Simulated results of the drop strength of chemical strengthened glass and lithium concentration in the molten salt during mass manufacturing.

4. Discussion

(1) Chemical species of precipitated salts

In the thermodynamic simulations, NaLiSO₄ was the only precipitated material expected upon the addition of sulfate. However, the X-ray diffraction analysis revealed the presence of Li₂NaK(SO₄)₂ as a stable lithium-containing solid in this system. Notably, this compound could not be included in the thermodynamic calculations because of the absence of the thermodynamic data in the database. If these thermodynamic data were available for the calculations, Li₂NaK(SO₄)₂ would have been the generated material. Therefore, Li₂NaK(SO₄)₂ is a reasonable lithium-containing material that results from a mixture of alkali nitrates and sulfates. Na₂SO₄, NaNO₃, and KNO₃ were adhered to the Li₂NaK(SO₄)₂ crystals as solvents.

Na₃(NO₃)(SO₄)·H₂O has been formed owing to moisture absorption while the collected solids were stored in the ambient atmosphere.

The collected solids contained 25,600 ppm lithium, which is approximately half the lithium concentration if the solids were entirely composed of Li₂NaK(SO₄)₂ (51,780 ppm). In this study, non-lithium-containing materials were detected by X-ray diffraction in addition to sulfates, including lithium. This suggested that the collected solids contained non-lithium-containing materials that could have reduced the lithium concentration in the collected solids during the CC process.

(2) Improvement of Li extraction efficiency by jig design

The lithium concentration of the molten salt was lowered and the compressive stress on the strengthened glass was enhanced through the CC process, which included jig immersion and cooling. During the CC process, Li-containing crystals emerged on the jig surface, particularly on the metal mesh surface. The interface between the molten salt and metal wire can be the origin of the target solids. Therefore, the larger surface area of the recovery jig facilitated the collection of more target solids through the CC process. Figure 9 shows a schematic representation of solid precipitation on the recovery jig. Solids tend to be generated to minimize the surface energy of the interface between the molten salt and stainless steel of the jig or crystals. The interface increases if solids precipitate on a straight surface. However, the interface can be reduced by generating solids in the crossing area. Therefore, the crystals are likely to cover the cross-points of the metal mesh wires to reduce the surface energy. Consequently, large crystals could grow on the metal mesh surface, avoiding the retention of significant amounts of molten salt. This indicated that the collected solids contained low nitrate levels and high lithium concentrations.

(3) Temperature design optimization

The CC process requires lowering the temperature of the molten salt during solid generation because the amount of precipitated solids increases with decreasing temperature. Generally, the mixture melts at a temperature lower than that of each material. This phenomenon enables the nitrate salt to melt at low temperatures by properly mixing sodium nitrate and potassium nitrate. However, no particles should remain in the molten salt at the strengthening temperature, even if all the deposited components cannot be completely removed from the salt. This means that the precipitation temperature should be lowered to recover a significant amount of the collected solids. However, there is a risk of surface defects caused by solid adhesion. Therefore, the process temperature must be designed such that the precipitation temperature is sufficiently low to improve the compressive stress of the strengthened glass and the strengthening temperature is sufficiently high to prevent any particles from remaining in the molten salt.

The design of the recovery jig and process temperatures enabled the efficient recovery of Li components by simply controlling the temperature of the molten salt without the risk of surface defects.

(4) Total system design

Figure 10 illustrates our proposed circular system for the chemical strengthening of salts and lithium. The deteriorated molten salt is separated into reused molten salt and solids with a higher lithium concentration than that of the molten salt through the CC process. The recycled molten salt was replenished with sodium nitrate and sodium sulfate to maintain a stable sulfate concentration and was used again as a chemical strengthening salt. This separation

process can replace the disposal of deteriorated salts and drastically reduce nitrate usage. Considering the adhesion of the molten salt to the glass during the chemical strengthening process, the total use of the chemical strengthening salt was approximately 10% of that in the conventional process.

Simultaneously, the solids collected from the separation process were dissolved in water and refined into lithium carbonate via purification using sodium carbonate. Lithium carbonate can be reused as a raw material for display cover glasses or lithium-ion batteries, enabling the circulation of lithium resources through the glass manufacturing processes. According to this concept, only a small amount of nitrate and sulfate from the purification process is wasted. Based on the experimental data under ideal conditions, this waste was calculated to be only 7.8 wt.% of the waste generated by the conventional strengthening process, which disposes of all deteriorated salt. Consequently, the CC process can contribute to the circular usage of lithium and the strengthening of salt, thereby significantly reducing waste from the glass manufacturing process.

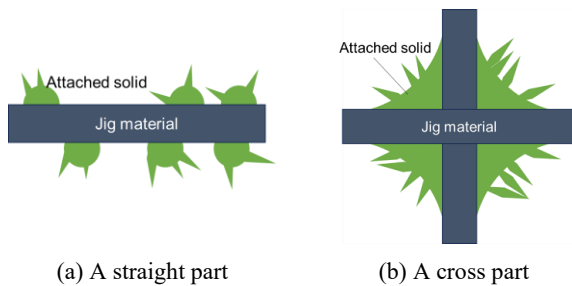


Figure 9. Schematics of crystal precipitation on the recovery jig.

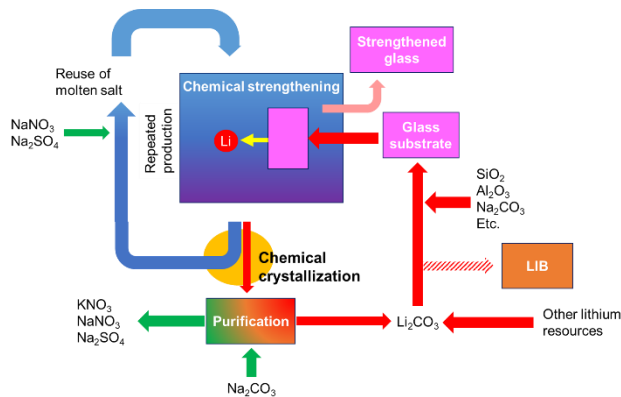


Figure 10. Circular system for lithium recycling and reuse of molten salt.

5. Conclusions

This study focused on the circular usage of lithium resources in the glass-strengthening process and demonstrated the separation of lithium from deteriorated chemical strengthening molten salt using the CC process.

Based on the thermodynamic equilibrium simulation results, sulfate was selected as the additive anion species, enabling the precipitation of lithium-containing crystals by cooling the molten salt to a particular temperature range.

To demonstrate the CC process, a metal mesh recovery jig was immersed in a simulated deteriorated molten salt, and the Li-

containing crystals were collected at the designed temperature. The lithium in the collected solids was concentrated to approximately three times that of the molten salt before the CC process. This increased the compressive stress of the strengthened glass compared with that before the CC process without causing any defects on the glass surface. The simulated fluctuations in the lithium concentration and compressive stress in the strengthened glass showed cyclic changes corresponding to the number of chemical strengthening cycles.

To recover lithium efficiently, the attached non-lithium-containing materials should be reduced and the amount of precipitated solids should be increased. An appropriate design of the recovery jig and temperature adjustment in the CC process are essential to achieve this purpose.

Based on these experimental results, a circular lithium system based on the CC process was proposed. The recovered lithium can be purified into lithium carbonate using existing processes, enabling its use as a raw material in glass and lithium-ion batteries. The system also facilitates the reuse of the strengthening salts. The obtained results indicate that the CC process is an appropriate method for achieving sustainable utilization of lithium resources in the mass manufacturing process.

Patent has been filed for this technology [11].

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