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Study on the Influence of Modified Roasting on the Leaching of Complex Aluminum Electrolyte

Jianfeng Hou Yutong Ma Yibing Cai Yiming Zhang Jiazhuo Zhang

Department of Chemistry and Chemical Engineering, Luliang University, Luliang

Abstract: Department of Chemistry and Chemical Engineering, Luliang University, Lyuliang Abstract: In this paper, modified roasting and leaching experiments were carried out on complex aluminum electrolytes containing Li. The effects of different modifiers, modified roasting time, and modified roasting temperature on the structural changes of the complex aluminum electrolyte and the Li leaching rate were studied. The experimental results show that when NaHSO4 is used as the modifier and roasted at 400°C for 180 minutes, Li in the complex aluminum electrolyte is converted from the insoluble Na_2LiAlF_6 phase to the soluble $LiHSO_4$ phase. The leaching rate of Li in the aluminum electrolyte increases from 2.01% to 72.45% with the change of modified roasting conditions.
Keywords: Modified roasting; Complex electrolyte; Leaching

1 Introduction

In recent years, with the rapid development of the aluminum electrolysis industry, a large amount of bauxite resources have been developed and utilized. Therefore, China's alumina industry uses a large number of low-grade bauxites for the production of industrial alumina. This kind of low-grade bauxite contains a certain amount of alkali metal oxides, especially in regions such as Henan and Shanxi, where the content of lithium oxide is higher than that in other producing areas. The content of lithium in the industrial alumina produced using this kind of bauxite can be more than 30 times that of foreign metallurgical-grade alumina. And this kind of industrial alumina containing lithium salts is widely used in the production of electrolytic aluminum in China (Abereaux A T, 1992; Yang J H et al., 2006; Yuril Z et al., 2007). When using this kind of alumina to produce aluminum, as it enters the aluminum electrolyte, the lithium in the alumina also enters the aluminum electrolyte and will continue to accumulate (Boulanger J & Gosselin A, 2022). With the continuous use of this alumina for production, the amount of lithium in the aluminum electrolyte will continue to increase, which will cause changes in the electrolyte structure, resulting in the typical solid waste in

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Corresponding author: Jianfeng Hou, Department of Chemistry and Chemical Engineering, Luliang University, Associate Professor
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the current aluminum electrolysis industry, i.e., complex aluminum electrolyte. Due to the changes in the proportion of various phase components in the complex aluminum electrolyte, it will cause a series of negative impacts on aluminum electrolysis production, such as reducing current efficiency, reducing the solubility of aluminum, and affecting the purity of aluminum (Fernandez R et al. 1985). At the same time, the addition of Li reduces the primary crystal temperature of the electrolyte and increases the electrolysis superheat (Cui C et al., 2023), and lithium has a very high destructive effect on the carbon materials in the electrolytic cell (Wang W et al., 2019). This is because the lithium ions in the complex aluminum electrolyte react with the carbon materials to form metallic lithium, which enters the carbon materials, causing expansion and damage to the carbon materials (Galasiu I et al., 2007; Li J et al., 2009). Therefore, problems such as excessively high electrolysis superheat and the reaction of lithium on carbon materials exist, which in turn lead to the corrosion and damage of the complex aluminum electrolyte to the electrolytic cell, shortening the service life of the electrodes and the electrolytic cell (Wang W et al., 2019).

At present, under the background of strict requirements on environmental protection issues, the development of green and environmentally friendly electrolytes has become the key to the sustainable development of the aluminum industry (Xu R et al., 2023). This kind of complex aluminum electrolyte, while affecting aluminum electrolysis production, has also become a solid waste in this field, which is obviously inconsistent with the current production requirements of low-carbon and environmentally friendly production. Therefore, removing or reducing the lithium element in the complex aluminum electrolyte is a hot research direction in the current aluminum electrolysis industry, which has very important practical significance.

Since the composition and structure of Li in the complex aluminum electrolyte are not suitable for leaching removal, this study adopts the modified roasting method. First, a modifier is used to change the composition and structure of Li into a structure suitable for leaching under certain roasting conditions, and then the effect of modified roasting on the leaching of the complex aluminum electrolyte is verified through leaching experiments. Thus, the purpose of solving the impact of the solid waste complex aluminum electrolyte in the aluminum electrolysis industry is achieved.

2 Experiments

2.1 Modified Roasting Experiment

2.1.1 Raw Material: Industrial Complex Aluminum Electrolyte

The raw material used in the experiment is industrial complex aluminum electrolyte, which is derived from a domestic 400kA electrolytic cell. Its composition is analyzed and tested by elemental analysis. Table 1 shows the components of the industrial complex aluminum electrolyte.

Table 1 Composition of industrial complex aluminum electrolyte sample (wt%)

No.	NaF	AlF_3	CaF_2	LiF	Al_2O_3	CR
Composition	49.22	38.01	3.22	4.94	2.24	2.60

2.1.2 Modified Roasting Experiment

A certain amount of industrial complex aluminum electrolyte sample is taken, mixed, and ground according to the molar ratio of Li ions in the electrolyte sample to Na ions in different modifiers being 1 ： 1. The ground sample is placed in a heating furnace for modified roasting experiments with different modifiers, different roasting times, and different roasting temperatures. XRD phase analysis and SEM scanning electron microscope analysis are performed on the samples before and after roasting to obtain the structural changes and surface morphology changes of Li in the complex aluminum electrolyte before and after modified roasting. The modified roasting experimental conditions are listed in Table 2, where t is the roasting time and T is the roasting temperature.

Table 2 Modified roasting experimental conditions

Experimental conditions					
Modifier	NaC_l	Na_2SO_4	$NaHSO_4$		
t/min	120	150	180	210	240
T/℃	250	300	350	400	450

2.2 Leaching Experiment

A sulfuric acid solution with a pH of 0 is prepared as the leaching agent for the leaching experiment. The samples obtained under various modified roasting conditions are subjected to leaching experiments using sulfuric acid with a pH of 0 at room temperature, a solid-liquid ratio of 1 ： 20, and a leaching time of 60 minutes. After the experiment, the leaching solution is made up to 200ml, and the Li ion concentration in the leaching solution is tested to calculate the leaching rate.

3 Results and Discussion

3.1 Effect of Modified Roasting on Leaching of Complex Aluminum Electrolyte

3.1.1 Effect of Different Modifiers on the Leaching of Complex Aluminum Electrolyte

Figure 1 shows the lithium ion leaching rate of the modified complex aluminum electrolyte obtained with different modifiers. The results are obtained by adding sodium chloride, sodium sulfate, and NaHSO4 as modifiers respectively, roasting at 300°C for 180 minutes to obtain the modified complex aluminum electrolyte, and then subjecting the modified and roasted samples to leaching experiments using sulfuric acid with pH zero at room temperature, a solid-liquid ratio of 1 ： 20, and a leaching time of 60 minutes.

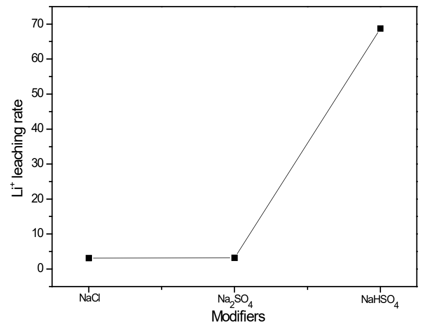


Figure 1 Lithium ion leaching rate of modified aluminum electrolyte obtained with different modifiers

It can be analyzed from Figure 1 that sodium chloride and sodium sulfate as modifiers contribute almost nothing to the leaching of lithium in the complex aluminum electrolyte, while the leaching rate of lithium in the modified complex aluminum electrolyte obtained with NaHSO4 as the modifier can reach 68.75%, indicating that NaHSO4 can modify Li in the electrolyte under this roasting condition to achieve the purpose of Li recovery and utilization.

3.1.2 Effect of Different Modified Roasting Times on the Leaching of Complex Aluminum Electrolyte

Figure 2 shows the lithium ion leaching rate of the modified complex aluminum electrolyte obtained with different modified roasting times. The results are obtained by adding NaHSO4 as the modifier, roasting at 300°C for 120, 150, 180, 210, and 240 minutes respectively to obtain the modified complex aluminum electrolyte, and after the roasting experiment, subjecting the modified and roasted samples to leaching experiments using sulfuric acid with pH zero at room temperature, a solid-liquid ratio of 1 ： 20, and a leaching time of 60 minutes.

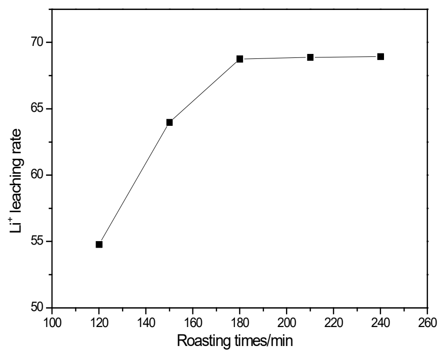


Figure 2 Effect of different modified roasting times on the leaching of complex aluminum electrolyte

It can be analyzed from Figure 2 that the modified roasting time has a certain influence on the leaching of the complex aluminum electrolyte. It can be found from Figure 2 that with the increase of modified roasting time, the leaching rate of lithium in the obtained modified complex aluminum electrolyte also increases. The leaching rate increases significantly during 120-180 minutes, and there is almost no change during 180-240 minutes. This is because the modification reaction of NaHSO4 on the complex aluminum electrolyte requires a certain reaction time, and the modification reaction is basically completed in 180 minutes. Therefore, the modified roasting time of 180 minutes can be selected as a suitable roasting condition for the modified roasting of the complex aluminum electrolyte.

3.1.3 Effect of Different Modified Roasting Temperatures on the Leaching of Complex Aluminum Electrolyte

Figure 3 shows the lithium ion leaching rate of the modified complex aluminum electrolyte obtained with different modified roasting temperatures. The results are obtained by adding NaHSO4 as the modifier, roasting at 200, 250, 300, 350, 400, and 450°C for 180 minutes to obtain the modified complex aluminum electrolyte, and after the roasting experiment, subjecting the modified and roasted samples to leaching experiments using sulfuric acid with pH zero at room temperature, a solid-liquid ratio of 1 ： 20, and a leaching time of 60 minutes.

It can be seen from Figure 3 that the modified roasting temperature has a very significant effect on the leaching of the complex aluminum electrolyte. Through the analysis of the obtained data, with the increase of the modified roasting temperature, the leaching rate of lithium shows an obvious increasing trend. The increase is relatively large in the temperature range of 200-400°C, while the leaching rate of lithium changes little when the temperature increases from

400 to 450°C. This indicates that when the complex aluminum electrolyte undergoes a modification reaction, a certain temperature and heat are required to achieve complete reaction. Before the modified roasting temperature increases to 400°C, the modification reaction gradually tends to be complete, so the leaching rate increases rapidly; while the leaching rate changes little after 400°C, indicating that when the roasting temperature reaches 400°C, the modification reaction of the aluminum electrolyte can basically be completed.

In summary, under the conditions of adding NaHSO4 as the modifier and roasting at 400°C for 180 minutes, the modification reaction of the complex aluminum electrolyte is basically complete, and the Li leaching rate in the obtained modified aluminum electrolyte can reach 72.45%, indicating that the structural modification of Li in the electrolyte under this modified roasting condition achieves the purpose of Li recovery and utilization.

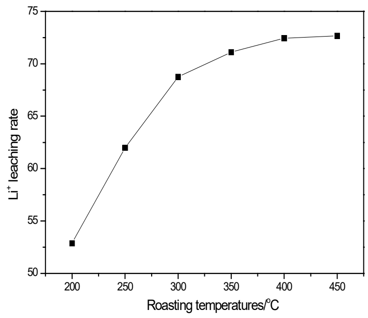


Figure 3 Effect of different modified roasting temperatures on the leaching of complex aluminum electrolyte

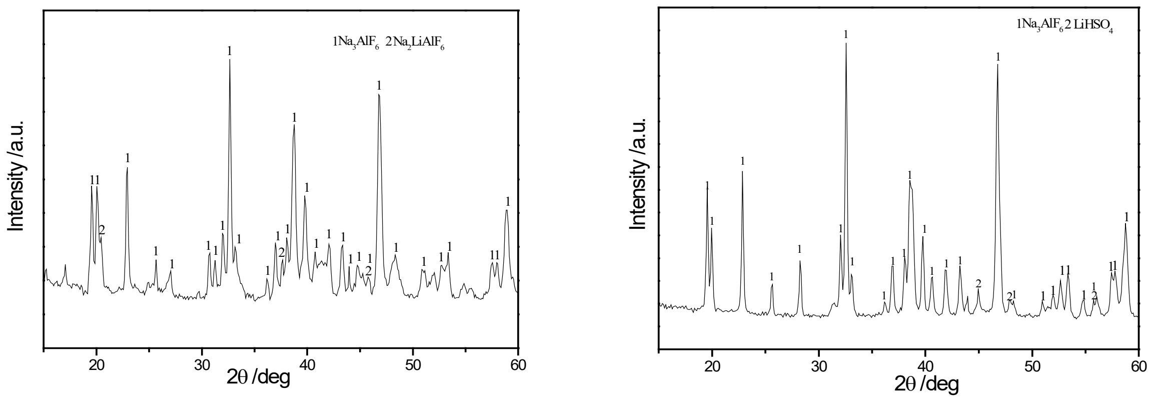
3.2 XRD Phase Analysis of Complex Aluminum Electrolyte Before and after Modified Roasting

From the experiment on the effect of modified roasting on the leaching of the complex aluminum electrolyte, it is found that the modification reaction is basically complete under the conditions of adding $NaHSO_4$ as the modifier and roasting at 400°C for 180 minutes. Therefore, the modified complex aluminum electrolyte obtained under these modification conditions and the raw material complex aluminum electrolyte are selected for comparative XRD phase analysis.

Figure 4 shows the XRD phase diffraction patterns of (a) raw material complex aluminum electrolyte and (b) modified complex aluminum electrolyte. It can be analyzed from the figure that before the modified roasting of the aluminum electrolyte, the main phase of the electrolyte is Na_3AlF_6, and the phase of Li is Na_2LiAlF_6. The characteristic peak of this phase is near the diffraction angle of 21°, and this composition structure belongs to the insoluble phase of lithium; after adding NaHSO4 and roasting at 400°C for 180 minutes, it is found that the Na_2LiAlF_6 phase peak of Li near the diffraction angle of 21° disappears, while a new phase characteristic peak appears near the diffraction angle of 45°, which is the $LiHSO_4$ phase. This indicates that after adding NaHSO4 for modified roasting, the phase structure of Li in the complex aluminum electrolyte changes, from the insoluble Na_2LiAlF_6 phase to the soluble $LiHSO_4$ phase, and the main phase in the electrolyte remains cryolite unchanged. Through phase analysis, it can be concluded that after modified roasting, the lithium phase in the complex aluminum electrolyte undergoes the following modification reaction:

$$Na_2LiAlF_6 + NaHSO_4 = Na_3AlF_6 + LiHSO_4$$

And under the conditions of adding NaHSO4 as the modifier with a Na^+: Li^+ molar ratio of 1 ： 1 and roasting the complex aluminum electrolyte at 400°C for 180 minutes, the modification reaction is basically complete.



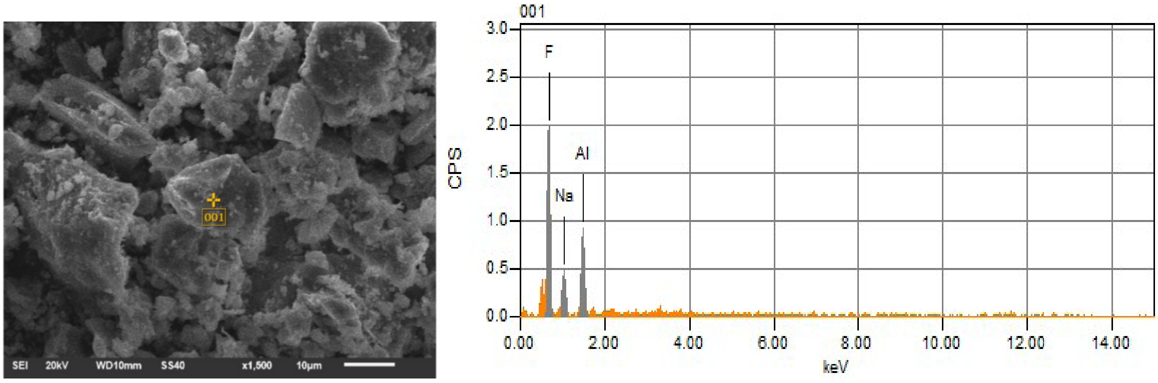
(a) Complex aluminum electrolyte (b) Modified complex aluminum electrolyte

Figure 4 XRD phase analysis of complex aluminum electrolyte before and after modified roasting

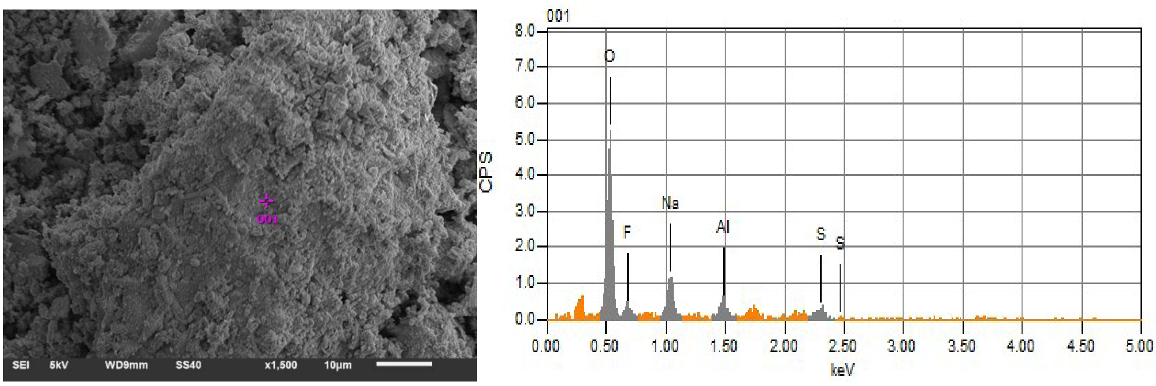
3.3 SEM Morphology Analysis of Complex Aluminum Electrolyte Before and After Modified Roasting

Figure 5 shows the SEM and EDS images of the complex aluminum electrolyte before and after modified roasting, where (a) is the raw material complex aluminum electrolyte and (b) is the modified complex aluminum electrolyte. It can be analyzed from Figure 5 that the structure of the complex aluminum electrolyte changes significantly before and after modified roasting. First, before modified roasting, observing under a magnification of 1500 times, it is found that the surface of the raw material aluminum electrolyte is smooth, and the particle size is about 10μm. EDS analysis shows that it is basically composed of elements such as F, Al, and Na, which is consistent with the result that the main structural component of the raw material aluminum electrolyte is cryolite Na_3AlF_6; after modified roasting, both the morphology and composition of the aluminum electrolyte change. First, its particle size increases to about 50μm, the surface becomes rough, and agglomeration occurs, and the aluminum electrolyte is wrapped and agglomerated with a large amount of newly generated substances. This is because during modified roasting, the aluminum electrolyte reacts with the modifier in a series of ways to form a modified aluminum electrolyte with a changed structure, and at the same time, under the action of high-temperature reaction, the newly formed substances are fused and agglomerated with each other to form a new morphological appearance. EDS analysis of it shows that the agglomerates are basically composed of elements such as F, Al, Na, O, and S, which have different compositions compared with those before modification. From the XRD phase analysis before and after roasting, it is known that lithium bisulfate, a sulfate substance, is formed after modification. Therefore, the EDS analysis after modification is consistent with the analysis result that, in addition to the cryolite structure, the modified aluminum electrolyte also has a sulfate structure.

In conclusion, it can be analyzed from Figures 4 and 5 that after adding NaHSO4 as the modifier and roasting at 400°C for 180 minutes, the complex aluminum electrolyte undergoes modification changes in both morphological structure and phase composition, forming a soluble phase of Li, i.e., $LiHSO_4$, which makes Li in the complex aluminum electrolyte soluble and achieves the purpose of recovery and utilization.



(a) Complex aluminum electrolyte



(b) Modified complex aluminum electrolyte

Figure 5 SEM and EDS images of the complex aluminum electrolyte before and after modified roasting

4 Conclusions

In this paper, modified roasting is used to change the structure of Li in the complex aluminum electrolyte, and the effect of leaching of the modified complex aluminum electrolyte is studied. The following conclusions are obtained through the research:

(1)Choosing NaHSO4 as the modifier, the leaching rate of Li in the complex aluminum electrolyte increases with the increase of roasting time and roasting temperature. The main reason is that the changes in the above conditions can increase the modification reaction rate of NaHSO4 on the complex aluminum electrolyte.

(2)Under the modified roasting conditions of adding NaHSO4 as the modifier with the molar ratio of Na ions in NaHSO4 to Li ions in the complex aluminum electrolyte being 1 ： 1, and roasting at 400°C for 180 minutes, the modification reaction is basically complete, and the leaching rate of Li in the obtained modified aluminum electrolyte can reach 72.45%;

(3)After modified roasting, the particles of the complex aluminum electrolyte become larger, the surface agglomerates, and in addition to the main cryolite structure, a sulfate structure appears.

(4)After modified roasting, the Li phase in the complex aluminum electrolyte changes, from the insoluble Na_2LiAlF_6 phase to the soluble $LiHSO_4$ phase. And the following modification reaction will occur:

$$Na_2LiAlF_6 + NaHSO_4 = Na_3AlF_6 + LiHSO_4$$

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