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RESEARCH ARTICLE

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Preparation of anhydrous magnesium chloride in a gas-solid reaction with ammonium carnallite

Abstract Dehydrated ammonium carnallite was synthesized with bischofite from salt lake and ammonium chloride solution in a 1:1 molar ratio of $MgCl_2$:NH_4Cl, dehydrated at 160°C for about 4 h. The yield was above 85%. The product was then mixed with solid-state ammonium chloride with a 1:4 mass ratio for the further dehydration at 410°C. The decomposition of NH_4Cl made a pressure of NH_3 at 30.5 kPa to prevent the hydrolysis of ammonium carnallite. The anhydration of magnesium chloride was achieved at 700°C. The results showed that anhydrous magnesium chloride contains magnesium oxide in an amount that was less than 0.1% by weight. XRD pattern and SEM micrograph showed a good dispersion of ammonium carnallite and anhydrous magnesium chloride crystals with well-distributed big grains, just enough to meet the need for the production of magnesium metal in the electrolysis process.

Keywords ammonium carnallite, gas-solid reaction, anhydrous magnesium chloride

As the lightest structural material, magnesium is found to have increasing applications in various areas [1–3]. The production methods of magnesium are mainly through thermal reduction and electrolysis. The thermal reduction process is an old process that has high energy consumption and causes severe pollution problems. In comparison, the electrolysis process shows some advantages, such as lower energy consumption and less pollution, which makes it a very promising technology [4–6]. Nowadays, above 80% magnesium is produced by the electrolysis process in the developed countries, while the thermal reduction process is widely adopted in our country. Some enterprises produce magnesium by the uncultured electrolysis process with magnesite, in which anhydrous magnesium chloride were obtained by chlorinating with coal [7–8]. The key to the electrolysis process is the high purity of the raw material, anhydrous magnesium chloride. There are abundant reserves of magnesium chloride in the salt lakes in Qinghai province of China. It can provide high grade raw materials for producing magnesium metal [9]. Normally, magnesium chloride exists as bischofite. Direct dehydration of bischofite does not lead to the production of high quality anhydrous magnesium chloride, because part of magnesium chloride may hydrolyze to magnesium hydroxide and the latter would then decompose to magnesium oxide, which has negative effects to electrolysis, i.e., reducing the current efficiency and eroding the electrode [10–13]. In order to obtain low magnesium oxide-containing anhydrous magnesium chloride to meet the need for the production of magnesium by electrolysis, we proposed a new process to prepare anhydrous magnesium chloride using bischofite from salt lake and ammonium chloride solution. Ammonium carnallite was prepared and dehydrated under hot air atmosphere. Dehydrated ammonium carnallite was mixed with an appropriate ratio of solid ammonium chloride, calcined at high temperature to produce anhydrous magnesium chloride. Ammonium chloride added to dehydrated ammonium carnallite in gas-solid reaction was decomposed into HCl and NH_3 at high temperature, NH_3 might substitute for the hygroscopic water of dehydrated ammonium carnallite and HCl would avoid the hydrolysis of magnesium chloride. Furthermore, ammonium chloride in the dehydrated ammonium carnallite after dehydration might also decompose into HCl and NH_3 during the calcination, which decrease the mass fraction of magnesium oxide in the production as well. In comparison to other processes for the preparation of magnesium chloride, this process was simple. Solid ammonium chloride can be recycled and anhydrous magnesium chloride obtained contained lower than 0.1% (in mass) MgO and can be used in the electrolysis process.

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1 Experimental

1.1 Reagents and instruments

Bischofite from a salt lake (contents: $MgCl_2$ 0.3526 $g \cdot g^{-1}$, K 0.1194 $g \cdot g^{-1}$, Na 0.0257 $g \cdot g^{-1}$, Ca 244.5 $\mu g \cdot g^{-1}$, S 247.1 $\mu g \cdot g^{-1}$); filtrate stock of deposit magnesium by ammonia (Contents: NH_4Cl:142.5 $g \cdot L^{-1}$, Mg 869 $mg \cdot L^{-1}$, K 371.7 $mg \cdot L^{-1}$, Na 326.6 $mg \cdot L^{-1}$, Ca 296.6 $mg \cdot L^{-1}$, S 131.9 $mg \cdot L^{-1}$); solid ammonium chloride (AR).

Rigaku 3,014 X-ray diffractometer (Japanese Rigaku Corporation); JEOL-5600LV scanning electron microscopy (Japanese JEOL Corporation); TGA/SDTA851^e thermal analysis system(American-Swiss Mettler Toledo Corporation); PS-6 vacuum ICP-AES (American Baird Corporation)

1.2 Methods

1.2.1 Preparative technology of ammonium carnallite

The solutions of bischofite from a salt lake (containing 3.877 $mol \cdot L^{-1}$ $MgCl_2$) and of ammonium chloride (containing 2.664 $mol \cdot L^{-1}$) were mixed at 1:1 molar ratio of $MgCl_2$ and NH_4Cl. After being heated to 80~85°C and constantly stirred for 1 h at pH 6.0, the mixture was cooled down to 6–8°C to crystallize. The yield of ammonium carnallite, after filtration and drying, was above 85%.

1.2.2 Dehydration of ammonium carnallite

Ammonium carnallite was dehydrated at 160°C under hot air atmosphere for 4 h to obtain dehydrated ammonium carnallite ($MgCl_2 \cdot NH_4Cl \cdot nH_2O$, n=0.5~1).

1.2.3 Preparative of anhydrous magnesium chloride

Dehydrated ammonium carnallite was mixed with a certain quantity of solid ammonium chloride and placed in resistance furnace. The mixture was heated at a certain temperature to get rid of H_2O in dehydrated ammonium carnallite, subsequently calcined at higher temperature to give anhydrous magnesium chloride.

1.2.4 Detection and characterization

ICP-AES was used to determine the contents of metallic and nonmetallic elements in anhydrous magnesium chloride; thermal analysis was conducted to determine the dehydration temperature of ammonium carnallite; titration analyses were used to determine the contents of magnesium chloride and magnesium oxide in the product; X-ray diffractometer and scanning electron microscopy were employed to study the composition and surface morphology of anhydrous magnesium chloride.

2 Results and discussion

2.1 TG-DTA analysis of ammonium carnallite and the determination of dehydration conditions thereof

Our results showed that anhydrous magnesium chloride prepared by dehydrated ammonium carnallite contained less magnesium oxide than that directly prepared by ammonium carnallite. Figure 1 shows TG-DTA curve of ammonium carnallite. The slight mass loss between 60°C and 110°C should be assigned to the evaporation of physically absorbed water on the particle surface. The mass loss (37.3%) between 110 and 180°C is due to the dehydration of $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$ to $MgCl_2 \cdot NH_4Cl \cdot nH_2O$. Since the theoretical mass loss due to the thermal decomposition of $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$ to $MgCl_2 \cdot NH_4Cl \cdot H_2O$ is 35.1%, it proved that $n<1$ in $MgCl_2 \cdot NH_4Cl \cdot nH_2O$. The mass loss within the range of 180°C to 340°C indicated $MgCl_2 \cdot NH_4Cl \cdot nH_2O$ continued to decompose and lose water. The hydrolysis of $MgCl_2$ might also contribute to the mass loss here, as magnesium chloride reacted with evaporating water to form magnesium hydroxide at high temperature. The mass loss at 340–430°C should correspond to the dehydration of dehydrated ammonium carnallite and the decomposition of ammonium chloride, 430–570°C the thermal decomposition from magnesium hydroxide to magnesium oxide hydrolyze from magnesium chloride. Under these conditions, ammonium carnallite lost almost all the crystal water but did not hydrolyze, resulting in the formation of dehydrated ammonium carnallite ($MgCl_2 \cdot NH_4Cl \cdot nH_2O$, n=0.5–1). If $n<0.5$ in dehydrated ammonium carnallite, magnesium chloride would partially hydrolyze after dehydration. If $n>1$, dehydrated ammonium carnallite was not completely dehydrated. As a result, during calcinations, the pressure fraction of H_2O originated from the substitution with NH_3 in the gas-solid reaction, would be so high that the magnesium chloride partially hydrolyzed, resulting in the

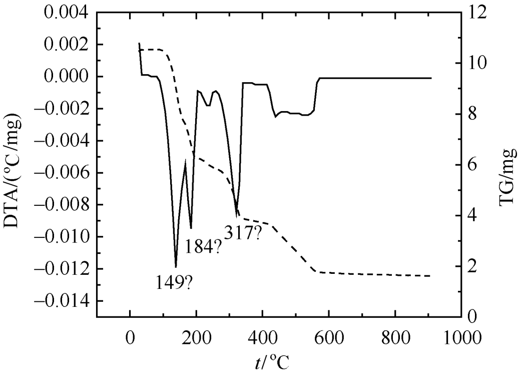

Fig. 1 TG-DTA curves of ammonium

Table 1 Mass percent of MgO in $MgCl_2$ at different n of $MgCl_2 \cdot NH_4Cl \cdot nH_2O$

n	<0.5	0.5~1	1~2.25	2.25~3.5	3.5~4.75	6
ω(MgO)/%	0.4	0.087	0.36	0.89	1.31	2.36

increase of the mass fraction of MgO in anhydrous magnesium chloride. The mass fractions of MgO in anhydrous magnesium chloride at 4:1 $NH_4Cl/MgCl_2 \cdot NH_4Cl \cdot nH_2O$ in mass ratio but different n of $MgCl_2 \cdot NH_4Cl \cdot nH_2O$ are given in Table 1.

2.2 Effect of quantity of solid ammonium chloride added to dehydrated ammonium carnallite on the content of MgO in anhydrous magnesium chloride

The mechanism of preparation of anhydrous magnesium chloride through a gas-solid reaction with low-water ammonium carnallite is discussed in this section. The solid ammonium chloride decomposed into ammonia and hydrogen chloride at the high temperature. Then, the ammonia substituted for the water in the low water ammonium carnallite to give the ammonation ammonium carnallite [14], which was calcined at high temperature to produce anhydrous magnesium chloride. Hydrogen chloride produced by the decomposition of ammonium chloride had two functions in the reacting system. Firstly, it might reduce the steam partial pressure in the gas phase, avoiding the hydrolysis of magnesium chloride. Secondly, hydrogen chloride might suppress the hydrolysis of magnesium chloride as well as the production magnesium oxide.

$$NH_4Cl=NH_3+HCl \qquad (1)$$

$$MgCl_2 \cdot NH_4Cl \cdot nH_2O+nNH_3=MgCl_2 \cdot NH_4Cl \cdot nNH_3+nH_2O \qquad (2)$$

$$MgCl_2+2H_2O=Mg(OH)_2+2HCl \qquad (3)$$

$$Mg(OH)_2=MgO+H_2O \qquad (4)$$

$$MgO+2HCl=MgCl_2+H_2O \qquad (5)$$

As the mixture of solid ammonium chloride and dehydrated ammonium carnallite was dehydrated and calcined under hot atmosphere without air, dehydration extended completely dependent on the pressure fraction of NH_3 in the system. In order to carry out reaction (2) completely, the pressure fraction of NH_3 must reach a special value in the gas–solid reacting system. And the NH_3 pressure fraction was related to the quantity of the solid ammonium chloride added to the system. Regarding the volume of the resistance surface engaged, the quantity of ammonium chloride as well as dehydration temperature, reaction (2) could take place completely only if the pressure fraction of NH_3 was above 30.5 kPa. As shown in Fig. 2, the mass fraction of magnesium oxide in anhydrous magnesium chloride were compared, which were obtained with mixtures of dehydrated ammonium carnallite and solid ammonium chloride in different ratios after dehydration at 410°C and calcination at 700°C. Along with the increase in mass ratio of solid ammonium chloride and low-water ammonium carnallite, anhydrous magnesium chloride obtained had less magnesium oxide. When the mass ratio was 4:1, the mass percentage of magnesium oxide in the anhydrous magnesium chloride is less than 0.001. If the mass ratio of the solid ammonium chloride and the low-water ammonium carnallite was too low, the production of NH_3 through the decomposition of solid ammonia chloride was insufficient, the substitution reaction (2) could not be carried out completely and part of magnesium chloride would hydrolyze during calcining at high temperature, resulting in the increase of the magnesium oxide content. Besides the quantity of ammonium chloride, the volume of resistance furnace also influenced the pressure fraction of NH_3 in the gas-solid system.

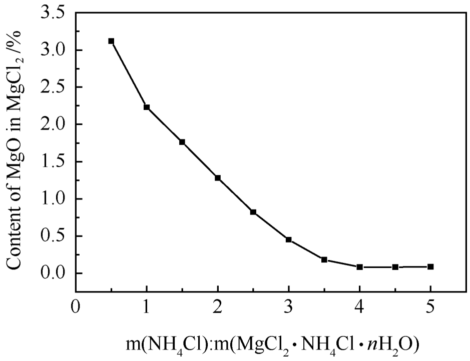

Fig. 2 Mass percent of MgO in $MgCl_2$ at different mass ratio of $NH_4Cl/MgCl_2 \cdot NH_4Cl \cdot nH_2O$ (n=0.5–1)

2.3 Effect of dehydration temperature and calcining temperature in gas-solid reaction with dehydrated ammonium carnallite and solid ammonium chloride on the content of magnesium oxide in anhydrous magnesium chloride

The reaction temperature for the preparation of anhydrous magnesium chloride through the dehydration of the mixtures of dehydrated ammonium carnallite and solid ammonium chloride at high temperature greatly affected the mass fraction of magnesium oxide in the product. Ammonium chloride should decompose in hydrogen chloride and ammonia before the mixture dehydrated at high temperature. Since the decomposition temperature of ammonium chloride is at 338°C, the dehydrating temperature of low water ammonium carnallite and the ammonia must be over 338°C. If the temperature was lower, ammonium chloride decomposed incompletely and the concentration of ammonia in the gas phase would be too low to complete substitution reaction. Thus, the obtained anhydrous magnesium chloride contains more magnesium oxide. On the other hand, if the temperature was higher, ammonia would emerge quickly from the solid into the gas without reacting with low-water ammonium carnallite, which also led to the increase of the magnesium oxide content in anhydrous magnesium chloride. The

Table 2 Mass percentage of MgO in $MgCl_2$ at different dehydrating and decomposing temperature

Dehydrating temperature/°C	Decomposing temperature/°C	W(MgO)/%
350	700	1.23
370	700	0.42
390	700	0.34
410	700	0.087
430	700	0.29
450	700	0.37
410	600	0.51
410	620	0.32
410	640	0.24
410	660	0.18
410	680	0.15
410	720	0.087
410	740	0.088
410	760	0.087

Table 3 Content of impurity elements in anhydrous magnesium chloride

Element	K	Na	Ca	B	Si	S
content/(μg/g)	1057.8	526.0	177.2	23.1	11.7	208.0

calcining temperature of ammonation ammonium carnallite also had influence on the quality of anhydrous magnesium chloride. While low temperature would cause the incomplete decomposition of ammonation ammonium carnallite, while high temperature would help to produce crude and even particles of anhydrous magnesium chloride, which would not get damp in the air. However, if the temperature surpassed 800°C, magnesium chloride would become steam and volatilize. Table 2 shows the mass percentage of magnesium oxide in anhydrous magnesium chloride at different dehydrating and decomposing temperatures. Our results proved that anhydrous magnesium chloride with the lowest magnesium oxide content and of crude crystal was obtained when the dehydrating temperature and decomposition temperature were at 410°C and 700°C, respectively. The contents of K, Na, Ca, Mg, B, Si, and S of anhydrous magnesium chloride obtained were determined with ICP-AES, as shown in Table 3. The result indicated these impurity elements do not affect the preparation of metal magnesium by electrolysis with anhydrous magnesium chloride [15].

2.4 XRD analysis

Figure 3 shows the XRD pattern of ammonium carnallite obtained by filtration and heating after bischofite from salt lake and ammonium chloride solution were mixed at 1:1 molar ratio of $MgCl_2$:NH_4Cl, stirred at 80–85°C for 1h with pH 6.0 and crystallized at 6–8°C. Figure 3 is the same as the standard XDR pattern of ammonium carnallite of XRD standard data bank JCPDS (PDF25-0039), which showed that ammonium carnallite obtained by this process contained no mix-phase of ammonium chloride. Figure 4 shows the XRD pattern of anhydrous magnesium chloride obtained by the gas-solid reaction. Compared with the standard XRD patterns of anhydrous magnesium chloride from JCPDS, the diffraction peaks were identical to each other, indicating that the prepared anhydrous magnesium chloride contained no. mix-phase. The titration analysis also showed that the content of anhydrous magnesium chloride was up to 0.999. The only difference is that the strongest diffraction peak in 2θ in the standard spectrogram was at 34.98°, while in anhydrous magnesium chloride it was at 15.11°. The reason for the existent differences might be that anhydrous magnesium chloride was prepared through different methods.

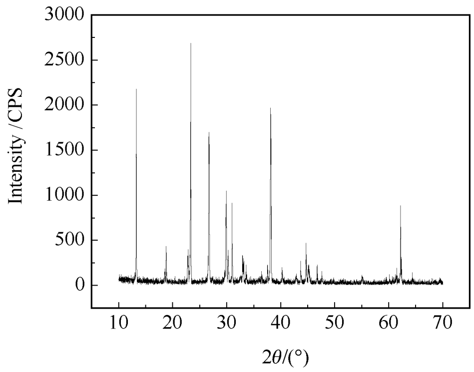

Fig. 3 XRD pattern of ammonium carnallite

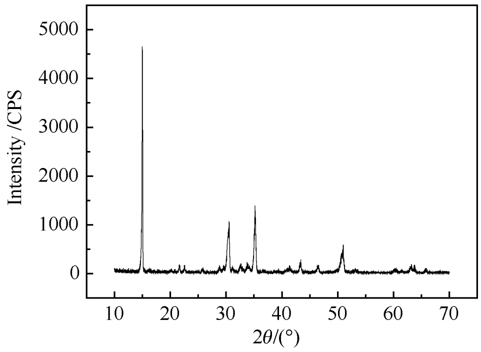

Fig. 4 XRD pattern of anhydrous magnesium chloride

2.5 SEM micrographs

The SEM micrograph of ammonium carnallite obtained is shown in Figure 5. Ammonium carnallite was of irregular polygon structure with obvious intergranular gap. The grain size was moderate, about 1 μm in average. Figure 6 show the SEM micrographs of anhydrous magnesium chloride, which was well-distributed, twinkling, big, flaky, polygonal crystal. The average particle sizes are over 0.6 μm.

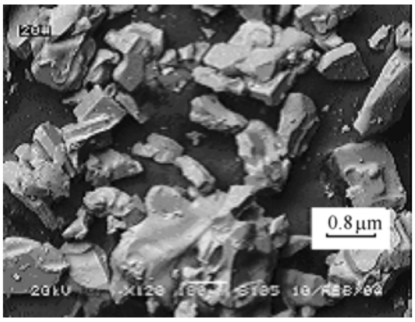

Fig. 5 SEM micrograph of ammonium carnallite

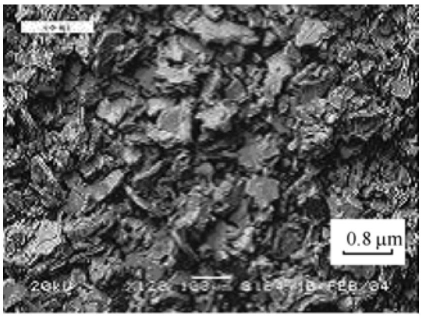

Fig. 6 SEM micrograph of anhydrous magnesium chloride

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