Article ID: 1003－7837(2005)02,03－0566－06

Synthesis of tetramethyl ammonium hydroxide by cell diaphragm electrolytic method

LI Xing-ying (李杏英), GU Heng (顾 珩), OUYANG Quan-sheng (欧阳全胜)

(Guangzhou Research Institute of Nonferrous Metals, Guangzhou 510651, China)

Abstract: Under the conditions of tetramethyl ammonia chloride (TMAC) used as starting material, Ti-based Dimensionally Stable Anode (DSA), stainless steel used as cathode and Nafion 900 cation membrane as cell diaphragm, this paper studies the synthesis of tetramethyl ammonium hydroxide (TMAH) by cell diaphragm electrolytic method, examining not only the effects of current density, concentration of starting material and cell temperature, on the product purity and current efficiency, but also the effects of electrolyte circulation rate on the service life of Ti-based DSA. The experiment puts forward an optimum processing condition, and experimental findings show that preparing TMAH by using this technique can obtain a current efficiency 74.7% and get product with a purity greater than 99.9%.

Key words: electrolytic method; tetramethyl ammonium hydroxide(TMAH); tetramethyl ammonia chloride (TMAC)

CLC number: TQ226.31 **Document code**: A

1 Introduction

Tetramethyl ammonium hydroxide (TMAH), as a very important catalyst, is used in synthesizing organosilicon products such as silicone rubber, silicone resin, silicone oil, etc.. The most widely applicable way to manufacture polysilicone is the ring-opening polymerization reaction of organic ring siloxane (short for D4) under the existence of TMAH. Dimethyl silicone polymer with hydroxide radical end-capped can be prepared, and its molecular weight can be controlled by this way, with a high outcome yield and an unsophisticated operation. Especially at the end of reaction, the stability of cross linked rubber can be guaranteed under the thermal decomposition of catalyst, instead of other additional extraction processes. There are many methods to prepare TMAH, such as the potassium hydroxide method, the silver oxide method, the electrolytic method, etc.. As for the potassium hydroxide method, it is a relatively traditional way with a simple technology and a low cost. Because the alkali metal ions inside can hardly be moved, the purity of the product is not high; since trace silver ion will be left inevitably with the silver oxide method, neither the quality nor the cost of TMAH prepared by this method can win the market; the electrolytic method appeared in the 1970s, which has a simple preparation technology, with a good quality and a low cost. In recent years, the technology of electrolytic method to prepare TMAH has gradually become well-rounded and

Received date: 2005－08－11

Biography: LI Xing-ying(born in 1968), Female, Engineer, Bachelor.

popularized in China[1-4]. According to the different sorts of cells, the electrolytic methods to prepare TMAH can be divided into mono-membrane method and multi-membrane method. On the basis of tetramethyl ammonia chloride (TMAC) used as starting materials, the electrolytic cell with two-chamber and one-membrane by using Nafion 900 cation ion exchange membrane as the cell diaphragm, this paper studied the technology to prepare TMAH.

2 Experimental

2.1 Materials

Materials for preparing TMAH were TMAC with chemical pure (Jintan Huadong Chemical Research Institute, China) and TMAH aqueous solution with reagent grade (Guangzhou Research Institute of Non-ferrous Metals, China). The quality specifications are in Table 1 and Table 2, respectively.

Table 1 Quality Parameters of TMAC (Mass fraction, %)

TMAC	H_2O	Unhindered amine and amine salt	Ash content
≥99.0	≤0.25	0.15	0.2

Table 2 Quality Parameters of TMAH aqueous solution (Mass fraction, %)

Alkali content	Impurity content					
	Fe^{3+}	Pb^{4+}	K^+	Na^+	Cl^-	Non-volatile matter
≥25	≤0.001	≤0.002	≤0.001	≤0.002	≤0.04	≤0.03

2.2 Experimental principle

In electrode reaction, ions in the electrolyte make directional motions under the action of electric field force. As cation exchange membrane is of permselectivity, anion can not transfer through it. Cl^- in anolyte discharges during the electrolytic process, but it can not enter into cathode space at the same time due to the block of cation exchange membrane. However, $(CH_3)_4N^+$ can go through the membrane into catholyte and get enriched in cathode chamber. In cathode chamber, water molecule can be decomposed into hydrogen and OH^- with equal equivalent weight. As OH^- can not go into anode space under the block of cation exchange membrane, it combines with $(CH_3)_4N^+$ in the cathode space and then $(CH_3)_4NOH$ comes into being. Through continuous circulation, $(CH_3)_4NCl$ in anode chamber is consumed step by step, while the concentration of $(CH_3)_4NOH$ in the catholyte is on the rise gradually. The electrode reactions are as follows:

Anode reaction: $2Cl^- - 2e \longrightarrow Cl_2 \uparrow$ (1)

Cathode reaction: $2H_2O + 2e \longrightarrow H_2 \uparrow + 2OH^-$ (2)

Overall reaction: $2(CH_3)_4NCl + 2H_2O \longrightarrow 2(CH_3)_4NOH + H_2 \uparrow + Cl_2 \uparrow$ (3)

2.3 Experimental method

Fig. 1 shows the schematic diagram of experimental unit. The cation exchange membrane used in Fig. 1 is the series of Nafion 900 membranes, with an effective area of 0.0376 m^2 (140 mm×340 mm). Ti-based Dimensionally Stable Anode (DSA) was used, and the cathode adopted stainless steel. Anolyte returns to anolyte encircling groove after being expelled chlorine and enriched, to maintain a certain concentration of

$(CH_3)_4NCl$ in the anolyte. $(CH_3)_4NOH$ is drawn from the catholyte after its concentration in the catholyte has reached a certain value. At the same time, ionized water is added to keep a certain concentration of $(CH_3)_4NOH$ in the cathode chamber.

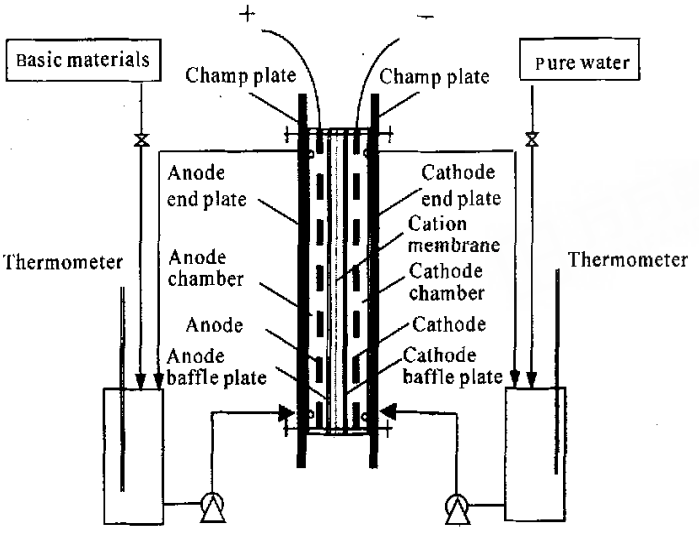

Fig. 1 Schematic diagram of experimental unit

The temperature of electrolyte is detected by mercury thermometer, and the cell voltage by HZ1943 digital multimeter. There is a periodic analysis to detect the concentrations of alkali and chloride ion during the electrolytic process. As for the analytical methods, the concentration of alkali can be titrated by standard hydrochloric acid solution with the indicator of methyl orange; the concentration of chloride ion can be determined by silver nitrate standard solution with potentiometric titration; foreign ions like Na^+ and K^+ can be analyzed by atomic absorption spectrophotometry; heavy metal ions can be determined by colorimetry.

3 Results and discussion

In order to find an optimum processing condition, we experimented on the factors of influencing on current efficiency and product purity, such as current density, concentration of starting materials and temperature of electrolysis. Furthermore, we also examined the effects on how electrolyte circulation rate works on the service life of Ti-based DSA.

3.1 Effects of current density on current efficiency and product purity

Under the conditions of the concentration of TMAC in anolyte as 2.75 mol/L, the concentration of TMAH in catholyte as 2.75 mol/L, and the temperature of electrolysis at 35℃, the effects of current density on current efficiency and product purity were examined and the results are in Table 3.

As can be seen in Table 3, along with the increase of current density, the current efficiency declines gradually. The reason for this is because the cell voltage increases and then the current drain ascends. The concentration of Cl^- in product TMAH solution, however, changes inconspicuously. Although the directional motion of Cl^- holds the dominant position under high electric field force, its diffusion motion is greatly subjected to inhibition. Of course, it is not the case that the lower current density is, the better the effect will be. If the current density descends, the production efficiency will be on the decline accordingly. Generally, the current density is controlled between 10 A/dm^3 and 15 A/dm^3 during the course of produc-

tion.

Table 3 Effects of current density on current efficiency and product purity

Current density/(A · dm^{-3})	Current efficiency/%	Concentration of Cl^- of TMAH/(mmol · L^{-1})
6	80.4	1.5
8	78.8	2.1
10	76.9	1.8
12	75.6	2.3
14	74.2	2.0

3.2 Effects of starting materials' concentration on current efficiency and product purity

Under the conditions of the current density as 13 A/dm^3, the concentration of TMAH in catholyte as 2.75 mol/L, and the temperature of electrolysis at 35℃, the effects of starting materials' concentration on current efficiency and product purity were examined and the results are in Table 4.

Table 4 Effects of starting materials' concentration on current efficiency and product purity

Starting materials/(mol · L^{-1})	Current efficiency/%	Concentration of Cl^- of TMAH/(mmol · L^{-1})
1.5	72.3	0.5
2.0	73.5	1.5
2.5	74.3	2.3
3.0	76.0	2.8
3.5	78.9	3.4

Table 4 shows, along with the increase of the starting materials' concentration, the current efficiency is also on the rise gradually. This is mainly because the electrical conductivity ascends and the resistance of electrolyte declines. Table 4 also shows that the concentration of Cl^- in product TMAH solution presents the upward trend with the rise of the starting materials' concentration, mainly due to the intensifying of diffusion motion of Cl^-.

3.3 Effects of temperature of electrolysis on current efficiency and product purity

Under the conditions of the current density as 13 A/dm^3, the concentration of TMAC in anolyte as 2.75 mol/L and TMAH in catholyte as 2.75 mol/L, the effects of temperature of electrolysis on current efficiency and product purity were examined and the results are in Table 5.

Table 5 Effects of temperature of electrolysis on current efficiency and product purity

Temperature of electrolysis/℃	Current efficiency/%	Concentration of Cl^- of TMAH/(mmol · L^{-1})
20	73.0	1.5
30	74.3	2.0
40	75.8	2.3
50	76.6	12
60	78.0	28

During the electrolytic process, part of electric energy may be translated into heat energy, leading to the temperature rise of electrolyte. It is found in Table 5 that, with the temperature rise of electrolyte, the current efficiency is on the rise gradually mainly because electrical conductivity ascends and the membrane

resistance declines, leading to the decline of current drain. When the temperature is below 40℃, the concentration of Cl^- in product TMAH solution increases a little with the temperature rise of electrolyte, mainly due to the intensifying of diffusion motion of Cl^-. But when the temperature is above 40℃, the concentration of Cl^- in product TMAH solution ascends rapidly with the temperature rise of electrolyte, mainly because the permselectivity of cation membrane to Cl^- weakens.

3.4 Effects of electrolyte circulation rate on the service life of Ti-based DSA

Under the conditions of the current density as 13 A/dm^3, the concentration of TMAC in anolyte as 2.75 mol/L, the concentration of TMAH in catholyte as 2.75 mol/L, and the temperature of electrolysis at 35℃, the effects of electrolyte circulation rate on the current efficiency and service life of Ti-based DSA were examined and the results are in Table 6.

Table 6 Effects of electrolyte circulation rate on the service life of Ti-based DSA

Electrolyte circulation rate/(L · h^{-1})	Service life of Ti-based DSA/day
0.70	5
1.35	7
6.75	More than 30

Experimental findings show that the electrolyte circulation rate has great effects on the service life of Ti-based DSA. The more the rate is, the longer the service life is. The reason for this is because the lower the rate is, the more easily the phenomenon of concentration polarization on anode appears. The phenomenon of concentration polarization has many disadvantages over electrolytic process, such as the rise of cell temperature and of current drain, and even directly reducing the service life of Ti-based DSA. On the contrary, the increase of circulation rate of electrolyte can eliminate the concentration polarization on anode, and it follows that the service life of anode is prolonged. If other conditions keep unchanging, the service life of anode will further influence on the service life of cation membranous. But it is not the case that the faster the circulation rate of electrolyte is, the better the effect will be, for the residence time the electrolyte stays in the cell will become shorter and the current efficiency will then decline. So it is very important to choose a proper electrolyte circulation rate. According to the experiment, a better rate is generally controlled between 6.5L/h and 6.75 L/h.

3.5 Synthetic experiment

From the above experiments, it is found that current density and electrolyte circulation rate are the main factors influencing on current efficiency, yet temperature has the biggest effect on product purity. Controlling the current density as 13 A/dm^3, the concentration of TMAC in anolyte as 2.75 mol/L, the concentration of TMAH in catholyte as 2.75 mol/L, and the temperature of electrolysis at 35℃, the electrolyte circulation rate as 6.5 L/h, and adopting the experimental unit in Fig. 1, the experimental results and current efficiency are listed in Table 7, after electrolyzing continuously for 30 days.

It is found in Table 7 that the results of synthetic experiment are relatively good. The concentration of Cl^- in TMAH solution is below 0.04%, and the concentration of Cl^- in product TMAH crystal can further decrease below 0.01% through concentration by evaporation, which has met the demand of synthesizing catalyst used in silicone rubber.

Table 7 Experimental finds in TMAH solution

Alkali content /%	Impurity content/%					Current efficiency /%
	Fe^{3+}	Pb^{4+}	K^+	Na^+	Cl^-	
23	0.003	0.002	0.003	0.002	0.025	74.7

4 Conclusions

(1) Under the conditions of Ti-based Dimensionally Stable Anode (DSA), stainless steel used as cathode and Nafion 900 cation membrane as cell diaphragm, current density and electrolyte circulation rate are the main factors influencing on current efficiency, yet temperature has the biggest effect on product purity.

(2) Electrolyte circulation rate has remarkable effect on the service life of Ti-based DSA. The higher the rate, the longer the service life.

(3) The optimum processing conditions with electrolytic method producing TMAH are: the ranges of the current density from 10A/dm^3 to 15 A/dm^3, the concentration of TMAC in anolyte from 2.5 mol/L to 3.0 mol/L, the concentration of TMAH in catholyte from 2.5 mol/L to 3.0 mol/L, the temperature of electrolysis from 35 to 40 ℃, and the electrolyte circulation rate from 6.5 L/h to 6.75 L/h. Adopting the experimental unit in Fig. 1, after electrolyzing continuously for 30 days, the concentration of Cl^- in product TMAH solution is below 0.04%. Through concentration by evaporation, the concentration of Cl^- may further decrease below 0.01%, which can meet the demand of synthesizing catalyst used in silicone rubber.

References

[1] Zhu X J, Chen Y S, Zhang X. S. The Preparation and purification of TMAH[J]. Jiangsu Chemical Industry, 2003, 31(5): 20−23.

[2] Wade R C. Electrolytic method for producing quaternary ammonium hydroxides[P]. US Pat: 4394226, 1983−06−19.

[3] Campbell C R, Spiegelhater R R. Preparation of quaternary ammonium hydroxides by electrolysis[P]. US Pat: 3402115, 1965−12−15.

[4] Eisenhauer R J, Pensacola. Process for electrolytic preparation of quaternary ammonium compounds[P]. US Pat: 3523068, 1966−12−19.