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Anion Effect on the Current Efficiency During the Preparation of Tetramethylammonium Hydroxide Solution by Electrolysis

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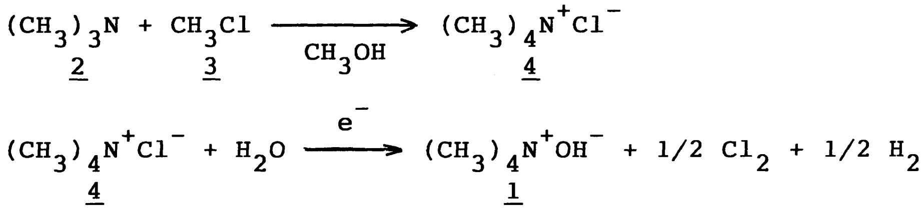
Tetramethylammonium hydroxide (TMAH) of high quality without corrosive ions were prepared by the electrolysis of the solution containing tetramethylammonium hydrogencarbonate (TMAC). Current efficiency varies by the anion of the tetramethylammonium salts and best with hydrogencarbonate among sulfate, chloride, and formate salts.

Tetramethylammonium hydroxide (TMAH) 1[1)] is widely used in developing and washing processes of semiconductor production. TMAH has been produced by the electrolysis of quarternary ammonium chloride 4 in an electrolytic cell equipped with a cation-exchange membrane as a diaphragm as shown in Scheme 1.[2)]



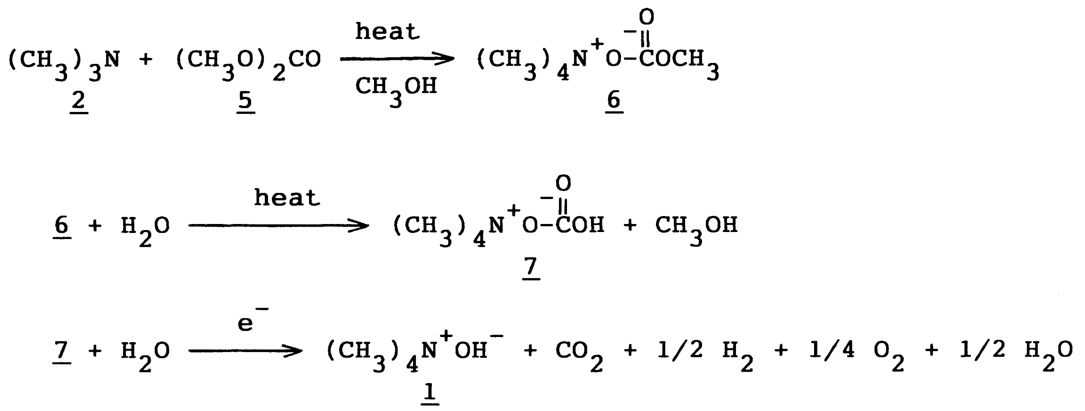
$$\underset{\underline{2}}{(CH_3)_3N} + \underset{\underline{3}}{CH_3Cl} \xrightarrow[CH_3OH]{} \underset{\underline{4}}{(CH_3)_4N^+Cl^-}$$

$$\underset{\underline{4}}{(CH_3)_4N^+Cl^-} + H_2O \xrightarrow{e^-} \underset{\underline{1}}{(CH_3)_4N^+OH^-} + 1/2\ Cl_2 + 1/2\ H_2$$

Scheme 1.

Recently, semiconductors have integrated more densely and this progress requires higher purity of TMAH. The corrosion by anions as well as cations is troublesome in a highly dense semiconductor. Particularly, small amount of chloride ion penetrates the cation-exchange membrane during the electrolysis and contaminates the hydroxide solution when the chloride 4 is used as a starting material. This contamination corrodes interconectors and semiconductor substrates and much effort has been made to prevent this invasion.[3)]

We have developed an industrial process for the production of a chloride free solution of TMAH by using tetramethylammonium formate,[4)] and further modified the method by using tetramethylammonium hydrogencarbonate (TMAC) 7 as shown in Scheme 2.[5)]



$$\underset{\underline{2}}{(CH_3)_3N} + \underset{\underline{5}}{(CH_3O)_2CO} \xrightarrow[CH_3OH]{heat} \underset{\underline{6}}{(CH_3)_4\overset{+}{N}\,\overset{-}{O}\text{-}\overset{O}{\overset{\|}{C}}OCH_3}$$

$$\underline{6} + H_2O \xrightarrow{heat} \underset{\underline{7}}{(CH_3)_4\overset{+}{N}\,\overset{-}{O}\text{-}\overset{O}{\overset{\|}{C}}OH} + CH_3OH$$

$$\underline{7} + H_2O \xrightarrow{e^-} \underset{\underline{1}}{(CH_3)_4N^+OH^-} + CO_2 + 1/2\ H_2 + 1/4\ O_2 + 1/2\ H_2O$$

Scheme 2.

In the last process hydrogencarbonate ion may penetrate the cation-exchange membrane and exist as carbonate ion in the TMAH solution. The carbonate ion comes also from cabon dioxide in the air during the operations, but the carbonate ion in TMAH solution is practically not corrosive and we now have a TMAH solution to meet the requirement for a fine semiconductor production.

When the chloride salt was subjected to electrolysis in the conventional manner, current efficiency decreases gradually. This phenomenon is attributed to the degeneration of the ion-exchange membrane (Nafion membrane).[6)]

Fortunately the electrolysis of TMAC 7 produced TMAH 1 efficiently without loss of current efficiency. Now we electrolyzed a variety of tetramethylammonium salts and studied the effect of anions on the current efficiency to clear whether the phenomenon is limited to chloride ion or not. Another purpose of this experiment is to discuss the above mentioned mechanism of the current efficiency drop.

The experiments were carried out in the following manner. The solution (484 g) containing 2.25 moles of TMAC was prepared as reported[5)] and neutralized by the treatment with 113 g of 98% sulfuric acid (1.13 moles), 104 g of formic acid (2.26 moles), or 228 g of 36% hydrochloric acid (2.25 moles). A solution of the ammonium salt obtained above was placed in an electrolytic chamber of polypropylene equipped with a cation-exchange membrane (Du Pont, Nafion 324[6)]) as a diaghragm. The chamber is equipped with a Ti-plate anode coated by IrO_2 and a cathode of stainless steel (SUS 304). A catholyte was 240 g of distilled water containing small amount of TMAH as an electrolyte. Electrolysis was performed by impressing 20 V between the anode and the cathode. The migration of tetramethylammonium ion ($(CH_3)_4N^+$) was monitored by the titration of the catholyte with 0.1 M hydrochloric acid solution using phenolphthalein as an indicator.

The correlation between the amount of the migrated tetramethylammonium ion and the consumed charge is shown in Fig. 1. A substantial decrease of the current efficiency was seen in the latter half period on the electrolyses of sulfate, chloride, and formate salts. However, we could see no decrease of current efficiency with the hydrogencarbonate salt and the linear relation between the migrated ammonium ion and the consumed charge was maintained until the final stage.

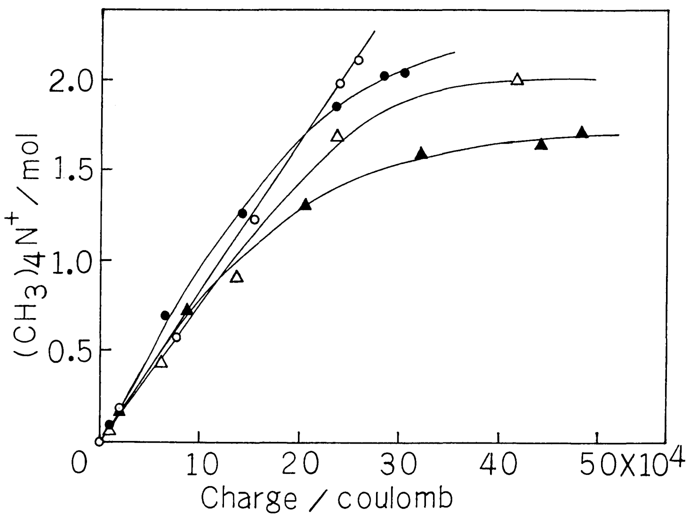


Fig. 1. Tetramethylammonium ion migration and the consumed charge (impressing 20 V). ○:Hydrogencarbonate,●:Formate, △:Chloride,▲:Sulfate.

Seko$^{7)}$ and Lowry and Maurits$^{8)}$ explained this degeneration as that the base-resin of Nafion has a non-bridged skeleton structure and the development of cation cluster of large volume around sulfonate groups modifies the skeletal structure of the Nafion membrane. This skeletal modification produces more hydrophilic domain in the membrane and a part of the hydroxide ions in the catholyte, which is originally prevented to penetrate by the electric field of sulfonate ions, moves into the anolyte to cause the decrease of current efficiency.

We justified these results as follows. When the chloride salt was electrolyzed, hypochloric acid (HClO) and hydrochloric acid are generated in the anolyte in addition to molecular chlorine (Cl_2). In the same manner, the sulfate and formate salt produce sulfuric acid ($SO_4^{2-} + H_2O - 2\ e = 1/2\ O_2 + H_2SO_4$) and formic acid ($HCOO^- - e = 1/2\ HCOOH + 1/2\ CO_2$), respectively. The electrolysis of TMAC <u>7</u> ($HCO_3^- - e = CO_2 + 1/4\ O_2 + 1/2\ H_2O$), however, produces no strongly acidic material. The acidity of the anode side increases by the progress of the electrolysis of the salts other than TMAC. As a result hydroxide ion in the catholyte becomes able to migrate to the anolyte through the membrane which now takes the relaxed structure as mentioned earlier. We must also consider the hydrogen ion transfer from the anolyte to the catholyte on the raise of hydrogen ion concentration. On the other hand, basic condition (pH=9-10) was kept in the anolyte at the electrolysis of TMAC and no decrease in the current efficiency was observed.

As seen in Fig. 1, the decrease in the current efficiency is more prominent with the stronger acid formed in the anolyte and it is realized that the important factor controlling the current efficiency is the pH of the anolyte.

Now we discovered the practical process for the production of TMAH of high quality by using TMAC as an intermediate and by the electrolysis of TMAC using a cation-exchange membrane. The TMAH produced in this process contains no corrosive anions and the current efficiency is superior compared to other salts of tetramethylammonium ion.

References

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