ELCTROLYTIC SYNTHESIS OF PERFLUOROTRIMETHYLAMINE WITH ALKALI METAL FLUORIDE CONTAINED CARBON ANODE

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ABSTRACT

The new carbon electrodes containing alkali metal fluorides such as LiF-CaF$_2$ and CaF$_2$ were developed to prevent the occurrence of anode effect in electrochemical fluorination and were used as the anode for electrolytic synthesis of perfluorotrimethylamine, (CF$_3$)$_3$N, from the mixed melt of (CH$_3$)$_4$NF·5HF and KF·2HF at 100°C. The ratio of (CF$_3$)$_3$N to the overall anode gas increased with increasing the concentration of (CH$_3$)$_4$NF and decreasing the current density and the best value of 61.7% was obtained in electrolysis of the mixed melt of (CH$_3$)$_4$NF·5HF (40 mol%) and KF·2HF (60 mol%) at 20 mA·cm$^{-2}$ with the 4 wt% CaF$_2$ contained carbon anode. However, the new carbon anode was broken down in the mixed melt of (CH$_3$)$_4$NF·5HF (50 mol%) and KF·2HF (50 mol%) during electrolysis. From these results, it is concluded that the alkali fluoride contained carbon is available as the anode for electrolytic production of (CF$_3$)$_3$N from the mixed melt having the molar fraction of KF higher than 0.143.

INTRODUCTION

(CF$_3$)$_3$N is expected to be a key material for synthesis of organic fluorocompounds such as a medicine and agricultural chemicals, because of releasing CF$_3$ radical. This compound is able to be obtained by electrolysis of trimethylamine, (CH$_3$)$_3$N, dissolved in anhydrous HF with the Ni anode [1]. In this case, temperature of electrolyte should be kept under 0°C during electrolysis and also the electrolytic cell should be equipped with a cooling tube to condense a gaseous HF carried together with the anode gas, because of the higher pressure of HF (ca. 50.6 kPa even at 0°C).

Recently, a new electrolyte, R$_x$NF·mHF (R = CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, and n-C$_4$H$_9$), was developed for partial fluorination of some aromatic compounds such as benzenes, toluenes, and xylenes with the Pt anode at room temperature [2~5]. When the Ni anode
is used, the electrolytic current observed in the \((CH_3)_4NF\cdot mHF\) melt was small compared with that in the mixed melt of \((CH_3)_4NF\cdot mHF\) and CsF\cdot 2HF. Although the addition of CsF in electrolyte is effective for increasing the electrolytic current, its cost is expensive. Hence, electrolysis of \((CH_3)_4NF\cdot mHF\) without additives is desirable for production in the industrial scale. For this purpose, a LiNiO\(_2\) coated Ni sheet electrode prepared by atmospheric plasma spraying technique was employed as the anode for electrolysis of \((CH_3)_4NF\cdot mHF\), and \((CH_3)_3N\) was obtained with the higher yield using it.

A new carbon electrode containing alkali metal fluoride was developed to prevent the occurrence of anode effect in fluorine production [6]. A carbon electrode may be able to use for electrolytic synthesis of \((CF_3)_3N\), because \((CF_3)_3N\) is permitted to be contaminated with CF\(_4\) evolved at the carbon anode. Use of alkali metal fluoride contained carbon anode was tried to develop a new process for electrolytic production of \((CF_3)_3N\). Since it is known that the molar fraction of KF in the mixed melt of NH\(_4\)F\cdot 2HF and KF\cdot 2HF should be higher than 0.233 for electrolytic production of NF\(_3\) with the carbon anode [7], the mixed melt of \((CH_3)_4NF\cdot 5HF\) and KF\cdot 2HF was used as an electrolyte in order to avoid the break-down of the carbon anode in this experiment.

This paper deals with effects of the KF-concentration in the mixed melt and the current density on the ratio of \((CF_3)_3N\) to the overall anode gas and the surface morphology of the alkali metal fluoride contained carbon after electrolysis.

**EXPERIMENTAL**

The cell employed for electrolytic production of \((CF_3)_3N\) was the cylindrical Ni cell (1.5 dm\(^3\)) as shown in Figure 1. The 4 wt% CaF\(_2\) contained carbon of 10 cm\(^2\) in surface area (Toyo Tanso Co., Ltd.) was employed as the anode. The anode was located at the center of cell whereas the cell wall was utilized as the cathode. The 4 wt% CaF\(_2\) contained carbon anode was dried at 130°C for longer than 24 hours in the vacuum desiccator before electrolysis. The Ni wire was used as the reference electrode in the mixed melt, which may act as Ni/NiF\(_2\) electrode. The potential of Ni/NiF\(_2\) reference electrode is 100 mV vs. H\(_2\) (hydrogen evolution potential). A nickel sheet skirt was provided between the anode and the cathode to separate the anode gas from hydrogen generated at the cathode, so that explosion is prevented. The cell bottom was covered with PTFE sheet to avoid hydrogen evolution.

The mixed melts of \((CH_3)_4NF\cdot 5HF\) and KF\cdot 2HF as shown in Table 1 were used as the electrolyte. Electrolysis was conducted at 20, 30, and 40 mA\cdot cm\(^{-2}\) with the nickel cell at 100°C. Although the water content was high before start-up, it might be decreased by electrolysis to less than 0.02 wt% at the end of experiment [8]. The anode gas was treated with NaF and alumina pellets to eliminate HF and F\(_2\) before the chromatographic and mass spectroscopic analysis (Shimadzu, GCMS-QP1000 and GC-14B). The ratios of the constituents in the anode gas were evaluated from the result of gas analysis.

The 4 wt% CaF\(_2\) contained carbon after electrolysis was used as the specimen for the SEM and XPS studies. The surface of the specimen was analyzed by XPS (Shimadzu, AXIS-165) and the surface morphology was observed by SEM (Hitachi, S-2460-N).
The apparatus for electrolytic synthesis of (CF$_3$)$_3$N.

**Table 1** Composition of electrolyte and molar fraction of component.

| Electrolyte | Molar fraction |
|-------------|----------------|
|             | (CH$_3$)$_4$NF | KF  | HF       |
| A           | 0.030          | 0.273 | 0.697   |
| B           | 0.056          | 0.222 | 0.722   |
| C           | 0.077          | 0.179 | 0.744   |
| D           | 0.095          | 0.143 | 0.762   |
| E           | 0.111          | 0.111 | 0.778   |

**RESULTS AND DISCUSSION**

**Anodic Polarization Curve by Cyclic Voltammetry**

In order to investigate the anodic behavior of the 4 wt% CaF$_2$ contained carbon electrode, its anodic polarization curve was observed in the mixed melts of (CH$_3$)$_4$NF·5HF and KF·2HF having the various concentrations of (CH$_3$)$_4$NF at 100°C by cyclic voltammetry with a sweep rate of 10 mV·s$^{-1}$ and the voltammograms obtained in the electrolyte C composed of (CH$_3$)$_4$NF·5HF (30 mol%) and KF·2HF (70 mol%) as an example are shown in Figure 2. A plateau at ca. 2 V and the following plateau in the potential range between 2 and 4 V appeared on the curve obtained in first run and they might be due to electrolysis of a trace of water in the melt and the formation reaction of graphite-fluorine intercalation compound, respectively [9]. In the range of potentials higher than 4 V, the anodic current due to the discharge of fluoride ion increased with increasing potential and then decreased acutely through the current peak at ca. 7 V, that is...
the anode effect occurred. The potential sweep measurement with the same specimen was repeated in the potential range of 0 V to ca. 8 V vs. Ni/NiF₂. The curve in second run differs from that in first run. The plateaus in the potential range between 2 and 4 V disappeared and this phenomenon means that the surface of the 4 wt% CaF₂ contained carbon anode was changed from an original carbon to the graphite-fluorine intercalation compounds [6,8,9]. Since the current peak was observed at ca. 6 V, the anode effect seemed to occur in the potential range over 6 V. The curve in 50th run was almost similar to that in second run.

![Graph showing anodic polarization curves](image)

**Figure 2.** Anodic polarization curves of the 4 wt% CaF₂ contained carbon electrode in the mixed melt of (CH₃)₄NF·5HF (30 mol%) and KF·2HF (70 mol%) at 100 °C by cyclic voltammetry with a sweep rate of 10 mV·s⁻¹.

**Surface Morphology of the 4 wt% CaF₂ Contained Carbon Anode After Electrolysis.**

Figure 3 is the SEM images of the 4 wt% CaF₂ contained carbon anode electrolyzed at 20, 30, and 40 mA·cm⁻² in the mixed melts of (CH₃)₄NF·5HF and KF·2HF at 100°C for 100 hours. The photographs in the second line are of the surfaces of the specimens after electrolysis in the electrolyte A composed of (CH₃)₄NF·5HF (10 mol%) and KF·2HF (90 mol%). The left, the center, and the right photographs are of those electrolyzed at 20, 30, and 40 mA·cm⁻², respectively. The top photograph is of the original surface of the specimen before electrolysis, which is shown as control. Those in the third, the forth, the fifth, and the bottom lines are of the specimens electrolyzed in the mixed melts of (CH₃)₄NF·5HF and KF·2HF with molar ratios of 20/80 (B), 30/70 (C), 40/60 (D), and 50/50 (E), respectively. The surfaces of the 4 wt% CaF₂ contained carbon anode after electrolysis were somewhat rough compared with that before electrolysis and no crack was observed on them except only one case using electrolyte E. The anode surface became rougher with increasing time of electrolysis. The 4 wt% CaF₂ contained carbon anode was broken down during electrolysis at 40 mA·cm⁻² in the electrolyte E composed of (CH₃)₄NF·5HF (50 mol%) and KF·2HF (50 mol%), in which the molar fraction was only 0.111 (see Table 1). The break-down of the carbon anode may be caused by lack of KF in the mixed melt.
Figure 4 shows the XPS spectra of C Is and F Is levels on the 4 wt% CaF₂ contained carbon anode polarized at 3 V and 7 V in the electrolyte C composed of (CH₃)₄NF•5HF (30 mol%) and KF•2HF (70 mol%) at 100°C. The upper spectra are of the specimen polarized at 3 V, and the lower spectra are of that at 7 V. The shoulder at 687.1 eV and a peak at 690 eV were observed on the F Is spectra for the specimen polarized at 3 V and they were assigned to the C-F semi-covalent and the C-F covalent bonds, respectively [8, 9]. In contrast, the shoulder at 687.1 eV disappeared on the F Is spectra for the specimen polarized at 7 V. That is, the anode surface is almost covered with the layer composed of the C-F intercalation compound with the covalent bond, which may cause anode effect. A peak at 287.8 eV on the C Is spectra for the specimen polarized at 7 V was assigned to the C-F covalent bond and was broad compared with that at 3 V. This also indicates that the surface of anode polarized at 7 V may be covered with the layer of the C-F intercalation compound having the covalent bond.

**Electrolytic Synthesis.**

Electrolysis of a mixed melt of (CH₃)₄NF•5HF and KF•2HF was conducted at 20, 30, and 40 mA·cm⁻² with the 4 wt% CaF₂ contained carbon anode. Temperature of the electrolyte was kept constant at 100°C during electrolysis. Anode potential in electrolysis of the various electrolytes was determined at 50 and 100 hours after switch-on and summarized in Table 2. Anode potential stayed in the potential range between 4.5 and 6.4 V, at which a fluoride ion can be discharged to form the atomic fluorine, and (CH₃)₄NF can be fluorinated to form (CF₃)₃N. Anode effect occurred during electrolysis at 30 and 40 mA·cm⁻² in the electrolyte E composed of (CH₃)₄NF•5HF (50 mol%) and KF•2HF (50 mol%), and then the anode was broken down, so that electrolysis could not be continued. Therefore, it is concluded that the 4 wt% CaF₂ contained carbon is useful as the anode for electrolytic production of (CF₃)₃N in the mixed melt of (CH₃)₄NF•5HF and KF•2HF having the molar fraction of KF higher than 0.143.

The anode gas was composed of CF₄, NF₃, C₂F₆, CHF₃, (CF₃)₃N, and so on. Table 3 shows the ratio of each constituent to the overall anode gas under each condition. The ratio of (CF₃)₃N to the overall anode gas increased with increasing the concentration of (CH₃)₄NF and decreasing the current density except the case of using the electrolyte E. The best ratio of (CF₃)₃N to the overall anode gas in this experiment was obtained in electrolysis at 20 mA·cm⁻² in the electrolyte D composed of (CH₃)₄NF•5HF (40 mol%) and KF•2HF (60 mol%) and its value was 61.7%.
**Before electrolysis.**

| Electrolyte | Current density |
|-------------|-----------------|
| (A) 10 mol%-(CH₃)₄NF · 5HF + 90 mol%-KF · 2HF | 20 mA · cm⁻² |
| (B) 20 mol%-(CH₃)₄NF · 5HF + 80 mol%-KF · 2HF | 30 mA · cm⁻² |
| (C) 30 mol%-(CH₃)₄NF · 5HF + 70 mol%-KF · 2HF | 40 mA · cm⁻² |
| (D) 40 mol%-(CH₃)₄NF · 5HF + 60 mol%-KF · 2HF |             |
| (E) 50 mol%-(CH₃)₄NF · 5HF + 50 mol%-KF · 2HF |             |

**Breakdown of Electrode**

**Figure 3.** SEM images of carbon anode before and after electrolysis at 20, 30, and 40 mA · cm⁻² in each mixed melt.
Figure 4. XPS spectra of C1s and F1s levels on 4 wt% CaF₂ contained carbon electrode after potentiostatic electrolysis at 3 V and 7 V in the mixed melt of 30 mol%-(CH₃)₄NF·5HF and 70 mol%KF·2HF at 100°C.

Table 2. Anode potential during galvanostatic electrolysis.

| Electrolyte                      | Current density (mA·cm⁻²) | Electric potential (V) |
|----------------------------------|---------------------------|------------------------|
|                                  | 50 hours                  | 100 hours              |
| A 10 mol%-(CH₃)₄NF·5HF + 90 mol%KF·2HF | 20                         | 5.2                    |
|                                  | 30                         | 4.8                    |
|                                  | 40                         | 6.3                    |
| B 20 mol%-(CH₃)₄NF·5HF + 80 mol%KF·2HF | 20                         | 4.6                    |
|                                  | 30                         | 5.0                    |
|                                  | 40                         | 5.2                    |
| C 30 mol%-(CH₃)₄NF·5HF + 70 mol%KF·2HF | 20                         | 4.5                    |
|                                  | 30                         | 5.7                    |
|                                  | 40                         | 5.7                    |
| D 40 mol%-(CH₃)₄NF·5HF + 60 mol%KF·2HF | 20                         | 5.1                    |
|                                  | 30                         | 5.1                    |
|                                  | 40                         | 4.8                    |
| E 50 mol%-(CH₃)₄NF·5HF + 50 mol%KF·2HF | 20                         | 5.3                    |
|                                  | 30                         | 5.9                    |
|                                  | 40                         | 5.3                    |
Table 3. The ratio of each gaseous constituent to the overall anode gas under each condition.

| Electrolyte      | Current density (mA cm⁻²) | NF₃ | C₂F₆ | CF₃NF₂ | (CF₃)₃N and/or (C₂F₅)₂ NCF | P | Other Gases |
|------------------|---------------------------|-----|------|-------|--------------------------|---|-------------|
|                  |                           |     |      |       |                          |   |             |
| A 10 mol%-(CH₃)₄NF-5HF | 20                         | 25.8| 33.5 | 1.6  | 18.9                     | 5.2| 8.3         | 6.7 |
|                  |                            | 23.4| 36.6 | 2.8  | 12.4                     | 1.5| 12.4        | 10.9|
|                  |                            | 26.8| 36.7 | 2.2  | 12.9                     | 6.1| 10.8        | 4.5 |
| B 20 mol%-(CH₃)₄NF-5HF + 40 mol%-KF-2HF | 20                         | 30.5| 11.6 | 1.3  | 39.8                     | 3.3| 11.0        | 2.5 |
|                  |                            | 23.6| 36.5 | —    | 17.2                     | — | 19.5        | 3.2 |
|                  |                            | 18.9| 48.1 | 3.0  | 10.2                     | 10.9| 14.4       | 2.5 |
| C 30 mol%-(CH₃)₄NF-5HF + 70 mol%-KF-2HF | 20                         | 8.9 | 17.3 | 2.0  | 44.8                     | 12.2| 10.9       | 3.9 |
|                  |                            | 26.3| 23.5 | 1.9  | 17.0                     | 13.1| 14.7       | 3.5 |
|                  |                            | 25.6| 29.3 | 1.4  | 10.4                     | 12.6| 17.5       | 3.2 |
| D 40 mol%-(CH₃)₄NF-5HF + 60 mol%-KF-2HF | 20                         | 15.4| 7.5  | 0.5  | 61.7                     | 5.7 | 12.2       | 2.2 |
|                  |                            | 33.3| 5.5  | 0.4  | 48.0                     | 0.1 | 10.6       | 2.1 |
|                  |                            | 22.6| 12.6 | 0.6  | 46.3                     | 6.9 | 9.6        | 1.5 |
| E 50 mol%-(CH₃)₄NF-5HF + 50 mol%-KF-2HF | 20                         | 36.9| 19.7 | 1.2  | 10.7                     | 5.8 | 21.3       | 4.4 |
|                  |                            | 30.8| 26.8 | 1.4  | 12.0                     | 7.6 | 19.7       | 1.8 |
|                  |                            | 27.7| 25.7 | 1.6  | 9.8                      | 10.4| 21.0       | 3.8 |

CONCLUSIONS

The cyclic voltammogram on the 4 wt% CaF₂ contained carbon and its surface analysis by XPS revealed that the anodic reaction may be divided into four regions as follows: (1) electrolysis of water at 1.0–2.0 V vs. Ni/NiF₂ (Region I) and formation of graphite-fluorine intercalation compounds at about 2.0–4.0 V (Region II) may take place; (2) the fluoride ion can be discharged on the 4 wt% CaF₂ contained carbon anode at potentials higher than 4.5 V (Region III); (3) the anode effect may occur over 7 V (Region IV) in the mixed melt of (CH₃)₄NF*5HF and KF·2HF. In the mixed melt having the KF molar fraction higher than 0.143, the 4 wt% CaF₂ contained carbon anode can be used for electrolytic synthesis of (CF₃)₃N without the break-down of the anode. The ratio of (CF₃)₃N to the overall anode gas tended to increase with increasing the concentration of (CF₃)₄NF in the mixed melt and decreasing the current density. In contrast, the ratio of (CF₃)₃N to the overall anode gas decreased and the break-down of the 4 wt% CaF₂ contained carbon anode occurred during electrolysis in the mixed melt of (CH₃)₄NF·5HF (50 mol%) and KF·2HF (50 mol%), in which the KF molar fraction was only 0.111. The best ratio of (CF₃)₃N to the overall anode gas in this experiment was obtained in electrolysis of the mixed melt of (CH₃)₄NF·5HF (40 mol%) and KF·2HF (60 mol%) at 20 mA cm⁻² and its value was 61.7%. From these results, it is concluded that the 4 wt% CaF₂ contained carbon is available as the anode for electrolytic synthesis of (CF₃)₃N from these mixed melts.
ACKNOWLEDGEMENTS

This work was supported by a grant to Research Center for Advanced Science and Technology at Doshisha University from the Ministry of Education, Japan.

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