

Electrolytic synthesis of perfluorotrimethylamine with alkali metal fluoride contained carbon anode

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Perfluorotrimethylamine, $(CF_3)_3N$, is expected to be a key material for synthesis of organic fluorocompounds, because of releasing CF_3 radical. This compound is able to be obtained by electrolysis of trimethylamine, $(CH_3)_3N$, dissolved in anhydrous HF with the Ni anode [1]. In this case, temperature of electrolyte should be kept under $0^\circ C$ 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 $0^\circ C$).

A new carbon electrode containing alkali metal fluoride was developed to prevent anode effect in electrochemical fluorination [2]. The carbon electrode is able to use for electrochemical synthesis of $(CF_3)_3N$, because $(CF_3)_3N$ is permitted to be contaminated with CF_4 evolved at the carbon anode. We tried to develop a new process of electrolytic production of $(CF_3)_3N$ using the alkali metal fluoride contained carbon anode. In order to avoid break-down of the carbon anode, the mixed melt of $KF \cdot 2HF$ and $(CH_3)_4NF \cdot 5HF$ was used as an electrolyte in this experiment.

A gaseous $(CF_3)_3N$ was obtained by electrolysis of the mixed melt of $KF \cdot 2HF$ and $(CH_3)_4NF \cdot 5HF$ at $100^\circ C$ with the 4 wt%- CaF_2 contained carbon anode. The ratio of $(CF_3)_3N$ to the overall anode gas under each condition was given in Table 1. In Table 1, the ratio of $(CF_3)_3N$ to the overall anode gas in electrolysis of the mixed melt of $KF \cdot 2HF$ (60 mol%) and $(CH_3)_4NF \cdot 5HF$ (40 mol%) at $30 mA \cdot cm^{-2}$ was 48.0% and its value was the largest in this experiment. The ratio of $(CF_3)_3N$ to the overall anode gas tended to increase with increasing the amount of $(CH_3)_4NF \cdot 5HF$ in the mixed melt and decreasing current density. The SEM image of the 4 wt%- CaF_2 contained carbon electrode before and after electrolysis at $30 mA \cdot cm^{-2}$ for 100h are shown in Figure 1. The surface of carbon anode after electrolysis was rough compared with that before electrolysis. However, no crack was observed on the surface of carbon anode after electrolysis. The cyclic voltammogram (Figure 2) indicates 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 production of graphite-fluorine intercalation compounds at about 2.0~4.0 V (Region II) may take place [3]; (2) the fluoride ion can discharge on the CaF_2 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 $KF \cdot 2HF$ (70 mol%) and $(CH_3)_4NF \cdot 5HF$ (30 mol%). From these result, it is concluded that the 4 wt%- CaF_2 contained carbon anode is available as the anode for electrochemical synthesis of $(CF_3)_3N$ in the mixed melt.

Table 1 Ratio of $(CF_3)_3N$ gas to overall anode gas under each condition.

Electrolyte	Ratio of $(CF_3)_3N$ gas in the anode gas (%)		
	Current Density ($mA \cdot cm^{-2}$)		
	40	30	20
10 mol%-TMA* + 90 mol%- $KF \cdot 2HF$	12.9	12.4	18.9
20 mol%-TMA* + 80 mol%- $KF \cdot 2HF$	10.2	17.2	39.8
30 mol%-TMA* + 70 mol%- $KF \cdot 2HF$	10.4	17.0	44.8
40 mol%-TMA* + 60 mol%- $KF \cdot 2HF$	46.3	48.0	-

Time of electrolysis : 50 hours
*TMA : $(CH_3)_4NF \cdot 5HF$

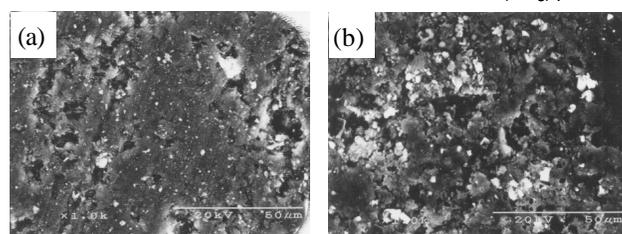


Figure 1 (a) SEM image of the 4 wt%- CaF_2 contained carbon electrode before electrolysis, (b) SEM image of the 4 wt%- CaF_2 contained carbon electrode after electrolysis at $30 mA \cdot cm^{-2}$ for 100h.

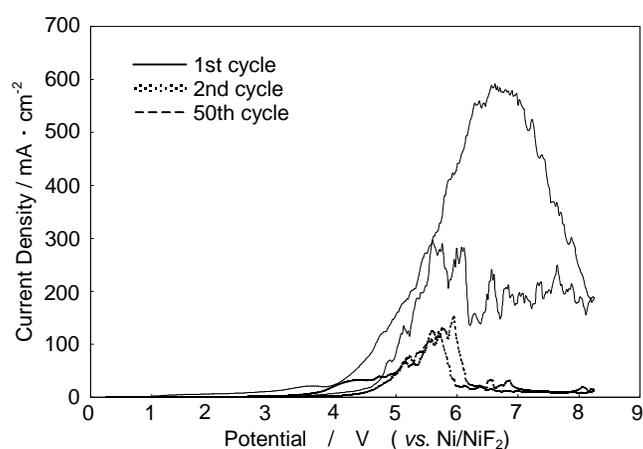


Figure 2 Anodic polarization curves of the 4 wt%- CaF_2 contained carbon electrode in the mixed melt of $KF \cdot 2HF$ (70 mol%) and $(CH_3)_4NF \cdot 5HF$ (30 mol%) at $100^\circ C$ by cyclic voltammetry with sweep rate of $10 mV \cdot s^{-1}$.

Reference

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