

Analysis of the species in the $(\text{CH}_3)_4\text{NF} \cdot m\text{HF}$ melt and electrolysis of its melt with LiNiO_2 coated Ni anode

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Perfluorotrimethylamine, $(\text{CF}_3)_3\text{N}$, is expected to be a key material for synthesis of organic fluorocompounds, because of releasing CF_3 radical. Recently, a new electrolyte, $\text{R}_4\text{NF} \cdot m\text{HF}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, \text{ and } n\text{-C}_4\text{H}_9$), was developed for partial fluorination of some aromatic compounds such as benzenes and xylenes with the Pt anode at room temperature^{1,2}. In order to develop a new process of electrolytic production of $(\text{CF}_3)_3\text{N}$, the $(\text{CH}_3)_4\text{NF} \cdot m\text{HF}$ melt was used as the electrolyte at room temperature.

In order to analyze the species in the melt prior to electrolysis, the $^1\text{H-NMR}$ and the IR measurements were conducted. $^1\text{H-NMR}$ spectra of $(\text{CH}_3)_4\text{NF} \cdot 3.5\text{HF}$ under various conditions were shown in Fig. 1. The signals at 1.9 and 2.8 ppm in Fig. 1a were assigned to protons in Acetonitrile and $(\text{CH}_3)_4\text{N}^+$ cation, respectively. On the other hand, the signal observed at 10.4 ppm in Fig. 1a suggest the existence of $(\text{HF})_n\text{F}^-$ ($n = 1, 2, \text{ and } 3$) ions. Although a free HF molecule and ions such as $(\text{HF})\text{F}^-$, $(\text{HF})_2\text{F}^-$, and $(\text{HF})_3\text{F}^-$ ^{3,4} should appear at different frequency, each signal for these species was not detected separately and only one sharp signal was observed, as shown in Fig. 1a. In order to divide this signal into each signal, the 0.1 M $(\text{CH}_3)_4\text{NF} \cdot 3.5\text{HF}$ dissolved in the polar solvent of D-Acetonitrile was measured and its result was shown in Fig. 1b. The signal assigned to $(\text{HF})_n\text{F}^-$ species was shifted to ca. 8 ppm and became broad. The signal of $(\text{HF})_n\text{F}^-$ observed at low temperature (-40°C) in Fig. 1c was much broader than that at room temperature. However, this signal was not yet divided separately. These facts suggest that a few signals may be combined due to the rapid exchange between some resonated species during NMR measurement. IR spectra of $(\text{CH}_3)_4\text{NF} \cdot m\text{HF}$ melts were shown in Fig. 2. When the m value of $(\text{CH}_3)_4\text{NF} \cdot m\text{HF}$ was more than 3.5, some broad peaks and a shoulder were observed, suggesting the existence of $(\text{HF})\text{F}^-$, $(\text{HF})_2\text{F}^-$ and $(\text{HF})_3\text{F}^-$ ions. The peak appeared at 3800 cm^{-1} and indicated the existence of a free HF molecule in the melts.

The molten salts having a lot of different m value ($m = 3.0, 3.5, 4.0, 4.5, \text{ and } 5.0$) were electrolyzed in order to investigate the effect of the HF concentration in the melt on the yield of $(\text{CF}_3)_3\text{N}$. Since it is known that the nickel based composite containing nickel oxide with the highly oxidation state was available as the anode material for electrochemical fluorination⁵, the LiNiO_2 coated Ni sheet was prepared by atmospheric plasma spraying technique and used as the anode. Fig. 3 shows the SEM image and XRD pattern of the LiNiO_2 coated Ni sheet. In electrolysis of the $(\text{CH}_3)_4\text{NF} \cdot m\text{HF}$ melt at 20 mA cm^{-2} for 100 hours with the LiNiO_2 coated Ni sheet, the ratio of Perfluorocompounds such as $(\text{CF}_3)_3\text{N}$, $(\text{CF}_3)_2\text{NC}_2\text{F}_5$, and $\text{CF}_3\text{N}(\text{C}_2\text{F}_5)_2$ to the overall anode gas tended to increase with increasing m value as given in Table 1.

In conclusion, we have successfully detected $(\text{HF})\text{F}^-$, $(\text{HF})_2\text{F}^-$, $(\text{HF})_3\text{F}^-$ and free HF molecule in this melt by the IR and $^1\text{H-NMR}$ measurements. Each ratio of these species was changed with increasing the m value. The ratio of free HF molecule in the melt may affect the ratio of Perfluorocompounds to the overall anode gas.

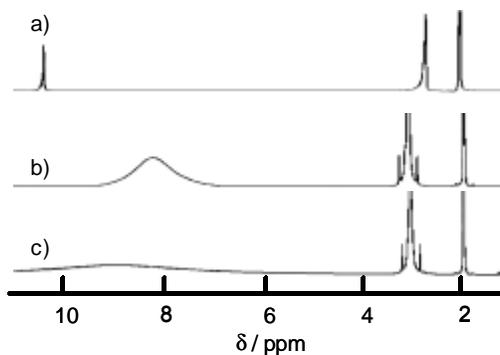


Fig. 1 $^1\text{H-NMR}$ spectra of $(\text{CH}_3)_4\text{NF} \cdot 3.5\text{HF}$.
a) : $(\text{CH}_3)_4\text{NF} \cdot 3.5\text{HF}$ shut in PFA tube at 25°C ,
b) : 0.1 M $(\text{CH}_3)_4\text{NF} \cdot 3.5\text{HF}$ + D-Acetonitrile at 25°C ,
c) : 0.1 M $(\text{CH}_3)_4\text{NF} \cdot 3.5\text{HF}$ + D-Acetonitrile at -40°C .

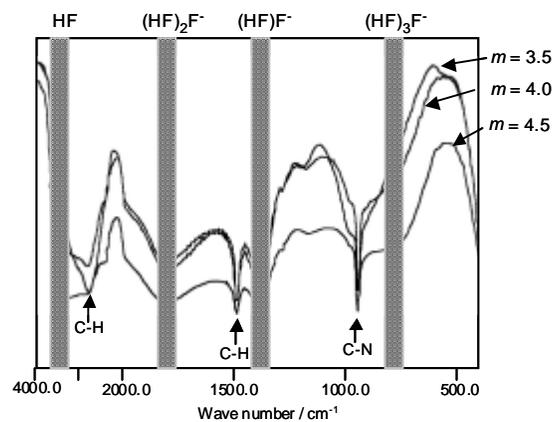


Fig. 2 IR spectra of $(\text{CH}_3)_4\text{NF} \cdot m\text{HF}$. $m = 3.5, 4.0 \text{ and } 4.5$.

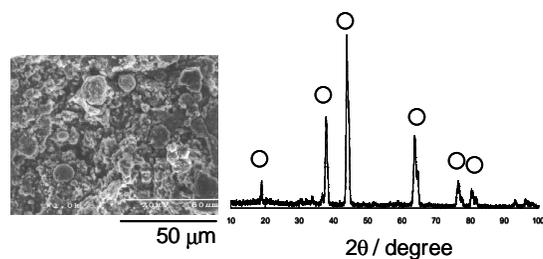


Fig. 3 SEM image and X-ray diffraction pattern of the LiNiO_2 coated Ni sheet prepared by atmospheric plasma spraying technique. \circ : LiNiO_2

Table 1 The constituents of evolved gas at the anode electrolyzed at 20 mA cm^{-2} for 100 hours in $(\text{CH}_3)_4\text{NF} \cdot m\text{HF}$ melt at room temperature.

m value	Ratio of Anode gas (%)					
	$\text{CF}_4 + \text{NF}_3$	C_2F_6	CHF_3	$(\text{CF}_3)_3\text{N}$	#	P
$m = 3.0^*$	59.31	3.07	2.73	25.46	1.53	7.90
$m = 3.5$	57.44	5.01	1.52	30.07	2.58	3.38
$m = 4.0$	53.13	4.74	1.79	33.11	5.62	1.61
$m = 4.5$	52.40	3.57	0.34	34.54	4.15	5.00
$m = 5.0$	52.91	5.32	1.01	32.23	6.73	1.80

Anode area : 5 cm^2 , $m = 3.0$; at 27°C
#: $(\text{CF}_3)_2\text{NC}_2\text{F}_5 + \text{CF}_3\text{N}(\text{C}_2\text{F}_5)_2$, P: Partial fluorinated compound

Reference

- K. Momota, M. Morita and Y. Matsuda, *Electrochimica Acta*, **38** (1993) 1123
- K. Momota, K. Mukai, K. Kato, and M. Morita, *Electrochimica Acta*, **43** (1998) 2503
- K. M. Haromon, and I. Gennick, *Journal of Molecular*, **45** (1977) 97
- A. Azman, M. Morita and Y. Matsuda, *Electrochimica Acta*, **38** (1993) 1123
- A. Tasaka, Y. Suzuki, S. Sakaguchi, N. Fukuda, and T. Tojo, *Electrochimica Acta*, **46** (2001) 4349