EFFECT OF METAL COMPLEX ION ADDED INTO A MOLTEN NH₄F·nHF ON THE CURRENT EFFICIENCY OF NF₃ FORMATION

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ABSTRACT

The anodic reaction on nickel electrode was carried out at 120°C in the molten NH₄F·2HF by a few kinds of electrochemical methods. AlF₃, NH₄NiF₃ and (NH₄)FeF₆ containing a small amount of (NH₄)FeF₆ were added into the melt in order to investigate the effects of these additives on the current efficiency of NF₃ formation and the anodic dissolution of Ni electrode. A Pt-rod was used as the reference electrode. The anode gas was quantitatively analyzed by both gas chromatography and infrared spectroscopy. With nickel anode, the passivation didn’t occur and the amount of anodic dissolution was about 4%. In electrolysis under the controlled current, the anode gas was composed of N₂, O₂, NF₃, N₂O, N₂F₂ and so on. The current efficiency was calculated from the flow rate of anode gas and its composition. The maximum current efficiency of NF₃ on Ni anode reached at 66% and then the anodic dissolution of Ni was only 3%. In the case of the addition of 0.1 mol% NH₄NiF₃ into the melt, the anodic dissolution of Ni electrode was about 1% and then the decrease in the current efficiency of NF₃ was only 6%. The greatest decrease in the current efficiency of NF₃ occurred in the melt added (NH₄)₂FeF₆. The addition of AlF₃ was not effective for the prevention of anodic dissolution of Ni. These results indicate that the addition of 0.1 mol% NH₄NiF₃ is favorable for the electrolytic production of NF₃.

INTRODUCTION

Nitrogen trifluoride (NF₃) is a stable gas at room temperature and has a strong oxidising action at higher temperature (1). Therefore, it has been already used as an oxidising agent for rocket fuels and a stable fluorinating agent (2-8). It may be also used as a welding agent for metals and a gas filler in order to increase the life and the brightness of lamps (9). Recently, a few researches have been attempted to develop the use of NF₃ as a laser gas (10-12), an etchant gas for a dry etching process (13-16) and a cleaner gas for apparatus used
in the CVD technique (17).

Some processes for the preparation of NF₃ have been proposed up to date, and the electrochemical process is better than the chemical process in the view point of the purity of NF₃, especially, free of CF₄ (18 - 21).

In earlier papers, we have reported on the electrolytic production of NF₃ from ammonium fluoride, urea and amides dissolved in a molten KH₂F₃ with a carbon electrode, and clarified the mechanism of electrochemical fluorination in this melt. But, in this procedure, NF₃ is contaminated with CF₄, because of the decomposition of (CF)n and/or (CxF)n [x > 2] film formed on the carbon electrode. On the contrary, nickel was the best material for the anode from the view point of both the production of NF₃ free of CF₄ and the anodic dissolution. However even a small amount of the loss of Ni anode increases the cost of the production of NF₃, and hence it is very important to prevent the anodic dissolution of Ni for the industrial production of NF₃. The addition of a metal fluoride or ammonium metal fluorides into the melt was attempted in order to prevent the anodic dissolution of Ni, and then the effect of additives on the current efficiency of NF₃-formation and the anodic dissolution of Ni was also investigated.

**EXPERIMENTAL**

One electrolytic cell of 1.5 dm³ in capacity was made of copper as shown in earlier papers (21 - 23) and another electrolytic cell of 0.45 dm³ in capacity made of polytetrafluoroethylene resin (teflon) as shown in Fig. 1. The rod of nickel with the surface area of 0.07 cm² was used as the anode for determination of polarization curves by the cyclic voltammetry and the anodic dissolution by the galvanostatic method. The plate nickel with the surface area of 10 or 66 cm² were also used for determination of the anodic dissolution of Ni and for the electrofluorination, respectively. The inside wall of the cell made of copper and a platinum wire were used as the cathode and the reference electrode, respectively. The inside wall of cell bottom was masked by teflon and the anode compartment of the cell was separated from the cathode compartment by a skirt of copper or teflon welded to the gas cover. The anode gas was passed through the absorption tube of gaseous HF filled with tablets of sodium fluoride (NaF) and then led to a gas-sampler. The sample gas was fractionated by gas chromatography and the fractionated samples, each corresponding to a distinct peak on the gas chromatogram, were identified by infrared spectroscopy.

The electrolyte was pre-electrolyzed at a low current density until NF₃ was detected, and then anodic polarization curves were determined by the cyclic voltammetry.
RESULTS AND DISCUSSION

The cyclic voltammograms on nickel in the molten NH\textsubscript{4}F-2HF were shown in Fig. 2. Two current peaks at about 0 V were observed on the anodic polarization curve. At the potential range between 0 and 6 V, the current density was very small. And then it increased again at the potential over 6 V. But the cathodic current peak was not observed at the potential below 3.0 V and the anodic current at potentials over 5 V increased with the number of cyclic scanning. From this result, it is concluded that nickel difluoride (NiF\textsubscript{2}) formed on nickel dissolves in the electrolyte to form complex ions, for example, NiF\textsubscript{n+}[n = 3 or 4] and/or Ni(NH\textsubscript{4})\textsubscript{m+}[m = 2 or 3] and no atomic fluorine adsorbs on nickel and/or nickel difluoride.

Figs. 3 and 4 showed the effects of added AlF\textsubscript{3} and NH\textsubscript{4}NiF\textsubscript{3} on the anodic polarization curves on nickel in the molten NH\textsubscript{4}F-2HF, respectively. In the addition of AlF\textsubscript{3}, the change in the shape of wave was not observed. On the contrary, the addition of NH\textsubscript{4}NiF\textsubscript{3} changed drastically the shape of wave; i.e., the first current peak at about -0.3 V disappeared on the anodic polarization curve after the addition of NH\textsubscript{4}NiF\textsubscript{3}, while the second current peak at about 0 V increased with increasing the concentration of the additive. These results indicate that nickel anode would be dissolved at the first peak to form Ni\textsuperscript{2+} and that the formed Ni\textsuperscript{2+} would be further oxidized at the second peak to form Ni\textsuperscript{3+}.

Fig. 5 showed the anodic polarization curves obtained by scanning the potential to the lower side from 9 V. The anodic current at the potential range between 5 and 8 V increased with increasing the concentration of NH\textsubscript{4}NiF\textsubscript{3}.

Fig. 6 showed the effect of the additive on the weight loss of Ni anode. In no additive, the same behavior as that in the addition of AlF\textsubscript{3} was observed. The effect of the NH\textsubscript{4}NiF\textsubscript{3}-concentration added into the melt on the weight loss of Ni anode during electrolysis was given in Table 1. From the figure and the table, it was found that the addition of only 0.1 mol\% NH\textsubscript{4}NiF\textsubscript{3} was effective enough for the prevention of anodic dissolution of Ni and that the ratio of quantity of electricity dissipated by anodic dissolution of Ni electrode to total quantity of electricity (\(Q/Q_t\)) decreased from 3 \% to only 1 \% by the addition of 0.1 mol\% NH\textsubscript{4}NiF\textsubscript{3}.

Fig. 7 showed the change of anode gas composition in electrolysis at the current density of 25 mA cm\textsuperscript{-2} as a function of time. NF\textsubscript{3} was already detected in the anode gas after electrolysis for only 7 hours and its composition ratio of anode gas, i.e. yield, increased with the lapse of time and reached the constant value of about 65 \%.

The flow rates of cathode gas composed of hydrogen only and anode gas composed of N\textsubscript{2}, O\textsubscript{2}, NF\textsubscript{3}, N\textsubscript{2}O, N\textsubscript{2}F\textsubscript{2}, and an unknown substance (N\textsubscript{2}F\textsubscript{2}? or N\textsubscript{2}F\textsubscript{3}) during electrolysis at the current density of 25 mA cm\textsuperscript{-2} were shown in...
Figs. 8 and 9, respectively. Both flow rates didn't decrease in the addition of AlF₃, while they decreased in the addition of NH₄NiF and (NH₄)₂FeF₆ containing a small amount of (NH₄)₄FeF₆. This fact indicates that the ions with the higher valence metal such as Ni³⁺ or Fe³⁺ would be reduced on the cathode to form the ions with the lower valence metal such as Ni²⁺ or Fe²⁺ and that the formed ions would be oxidized on the anode to form the original ions.

Table 2 showed the effect of NH₄NiF concentration on the yield of each product in the anode gas. This table revealed that the addition of NH₄NiF decreased the yield of NF₃. It is concluded, therefore, that the concentration lower than 0.1 mol% NH₄NiF is favorable for the electrolytic production of NF₃ in the view point of both the increment of the yield of NF₃ and the prevention of anodic dissolution of Ni.

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Fig. 1 Experimental apparatus for determination of anode polarization curve

Fig. 2 Anodic polarization curves on nickel electrode at 120°C in NH₄F·2HF by potential sweep method with sweep rate of 0.2 V·s⁻¹.
1: No addition of AlF$_3$
2: 0.2 mol% AlF$_3$
3: 0.4 mol% AlF$_3$

Fig. 3 Anodic polarization curves on nickel electrode in electrolyte of NH$_4$F·2HF + AlF$_3$ at 120°C by potential sweep method with sweep rate of 20 mV·s$^{-1}$ (First run)

1: No addition of NH$_4$NiF$_3$
2: 0.1 mol% NH$_4$NiF$_3$
3: 0.2 mol% NH$_4$NiF$_3$

Fig. 4 Anodic polarization curves on nickel electrode in electrolyte of NH$_4$F·2HF + NH$_4$NiF$_3$ at 120°C by potential sweep method with sweep rate of 20 mV·s$^{-1}$ (First run)
Fig. 5 Effect of added $\text{AlF}_3$, $\text{NH}_4\text{NiF}_3$ or $(\text{NH}_4)_2\text{FeF}_6$ on anodic polarization curves on nickel electrode at 120°C in $\text{NH}_4\text{F}_2\text{HF}$ by potential sweep method with sweep rate of 0.2 V·s$^{-1}$ (30th run)

1: No additive, 2: 0.8 mol% $\text{AlF}_3$, 3: 0.4 mol% $\text{NH}_4\text{NiF}_3$, 4: 0.8 mol% $\text{NH}_4\text{NiF}_3$, 5: 0.06 mol% $(\text{NH}_4)_3\text{FeF}_6$.

Fig. 6 Relationship between ratio of quantity of electricity dissipated by anodic dissolution of nickel electrode to total quantity of electricity ($Q_a/Q_t$) at 120°C and current density of 25 mA·cm$^{-2}$ and concentration of $\text{AlF}_3$ or $\text{NH}_4\text{NiF}_3$ in $\text{NH}_4\text{F}_2\text{HF}$
Table 1  Effect of added NH$_4$NiF$_3$-molar concentration on weight loss of nickel anode in electrolysis

| NH$_4$NiF$_3$ (mol%) | C.D. (mA·cm$^{-2}$) | E.D. (hrs.) | Potential (V vs. Pt) | number of electron |
|----------------------|----------------------|-------------|----------------------|-------------------|
| 0                    | 25                   | 97          | 4.4±5.1              | 2                 |
| 0.1                  | 25                   | 74          | 4.2±6.9              | 2                 |
| 0.2                  | 25                   | 76          | 5.0±5.5              | 2                 |
| 0.4                  | 25                   | 74          | 5.2±5.9              | 2                 |
| 0.8                  | 25                   | 50          | 5.2±5.9              | 2                 |

| Calculation weight loss of anode (g) | Observed weight loss of anode (g) | R.D. (%) |
|-------------------------------------|-----------------------------------|----------|
| 26.161                              | 0.7330                            | 2.80     |
| 17.387                              | 0.7330                            | 4.20     |
| 20.260                              | 0.1636                            | 0.81     |
| 13.507                              | 0.1636                            | 1.21     |
| 20.990                              | 0.1391                            | 0.66     |
| 13.993                              | 0.1391                            | 0.99     |
| 20.594                              | 0.1693                            | 0.82     |
| 13.729                              | 0.1693                            | 1.23     |
| 18.860                              | 0.1180                            | 0.63     |
| 12.573                              | 0.1180                            | 0.94     |

Headings; C.D.: Current density, D.E.: Duration of electrolysis, R.D.: Ratio of quantity of electricity dissipated by anodic dissolution of nickel electrode to total quantity of electricity ($Q_a/Q_t$)

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Fig. 7 Change of anode gas composition in electrolyte of NH$_4$F·2HF as a function of time

Fig. 8 Change of current efficiency of H$_2$ evolution in electrolyte of NH$_4$F·2HF containing added AlF$_3$, NH$_4$NiF$_3$ or (NH$_4$)$_3$FeF$_6$ as a function of time
1: calculated curve,
2(○): no additive,
(●): 1.0 mol% AlF$_3$,
(●): 2.0 mol% AlF$_3$,
3(□): 0.1 mol% NH$_4$NiF$_3$,
4(■): 0.2 mol% NH$_4$NiF$_3$,
5(△): 0.05 mol% (NH$_4$)$_3$FeF$_6$

Fig. 9 Change of flow rate of anode gas in NH$_4$F•2HF containing added AlF$_3$, NH$_4$NiF$_3$ or (NH$_4$)$_3$FeF$_6$

Table 2 Effect of AlF$_3$, NH$_4$NiF$_3$ and (NH$_4$)$_3$FeF$_6$—molar concentration on each current efficiency of anode gas products

| Additive | mol% | Current efficiency of anode gas products(%) |
|----------|------|---------------------------------------------|
|          |      | NF$_3$ | N$_2$ | O$_2$ | N$_2$O | N$_2$F$_2$ | X(N$_2$F$_4$?) | Total |
| -        | -    | 65.5   | 20.1  | 3.3   | 3.5    | 2.9        | 0.8      | 96    |
| AlF$_3$  | 1.0  | 68.3   | 22.2  | 0.3   | 1.4    | 3.2        | 1.1      | 97    |
| AlF$_3$  | 2.0  | 66.7   | 21.8  | 0.2   | 2.9    | 4.1        | 1.0      | 97    |
| NH$_4$NiF$_3$ | 0.1 | 59.8   | 20.9  | 3.8   | 1.0    | 3.1        | 0.9      | 90    |
| NH$_4$NiF$_3$ | 0.2 | 36.0   | 17.0  | 5.8   | 1.0    | 1.6        | 0.7      | 62    |
| (NH$_4$)$_3$FeF$_6$ | 0.05 | 49.8   | 15.3  | 2.9   | 0.5    | 2.9        | 1.2      | 73    |

Conditions: Anode; nickel( 66cm$^2$ ), Current density; 25mA·cm$^{-2}$, Temperature; 120°C