EFFECT OF METAL IMPURITIES ON ANODIC REACTION OF NICKEL ELECTRODE IN A MOLTEN NH$_4$F-HF SYSTEM

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ABSTRACT

The effects of metal impurities added and dissolved from a cell on both the anodic dissolution of a nickel electrode and the current efficiencies of NF$_3$-formation and total anode gas were studied in molten NH$_4$F-2HF at 120°C by galvanostatic electrolysis. The current loss caused by anodic dissolution of nickel in a copper cell (3.5%) was larger than those in a steel cell (1.5%) and a nickel cell (2.5%). Mixed gas composed of N$_2$, O$_2$, N$_2$O, NF$_3$, N$_2$F$_4$ and N$_2$F$_2$ was liberated at the nickel anode during electrolysis at 25 mA/cm$^2$. Copper ion almost unaffected the current efficiencies of NF$_3$-formation (60%) and total anode gas (90%), while iron and nickel ions decreased them. The existence of water in the melt lowered the anodic dissolution of nickel electrode. The addition of complexes such as NH$_4$NiF$_3$ and (NH$_4$)$_3$FeF$_6$ in the melt was also effective for prevention of the anodic dissolution of nickel, but it decreased the current efficiencies of NF$_3$-formation and total anode gas. Therefore, it is concluded that heavy metal impurities, especially Ni and Fe compounds, in the electrolyte are detrimental to the reaction proposed.

INTRODUCTION

Highly pure nitrogen trifluoride (NF$_3$, 99.99%) free from carbon tetrafluoride (CF$_4$) is mainly produced by electrolysis of molten NH$_4$F-2HF with a nickel anode. However, the high consumption of nickel anode is troublesome for this process. The corrosion of nickel anode results in electrolytic current losses of 3~5% at 120°C, resulting in deposition of nickel compounds such as NH$_4$NiF$_3$ and NiF$_2$ on the cell bottom.
and increases operating cost. Also, the corrosion rate is unaffected by the addition of LiF into the melt (1).

The objective of this work is to analyze the metal impurities in the melt dissolved from cells made of copper, steel and nickel and to investigate the effects of metal impurities on both the anodic dissolution of nickel and the current efficiencies of $\text{NF}_3$-formation and total anode gas.

**EXPERIMENTAL**

Three kinds of cylinder-type cells made of copper, steel and nickel (ca. 1.5 dm$^3$ volume) were provided for production of nitrogen trifluoride. Another H-type cell made of PTFE (ca. 1 dm$^3$ volume) was also provided for investigation of the effect of the additives such as $\text{NH}_4\text{NiF}_3$ and $(\text{NH}_4)_3\text{FeF}_6$ on the current efficiencies of $\text{NF}_3$-formation and total anode gas. The cell configuration was described in the previous papers (2, 3) in detail. A nickel sheet anode having the effective area of 24 cm$^2$ was located at the center of each cell through the cell cover. The inside wall of each cell was used as the cathode in a metal cell and a large-area nickel cathode was also used in a PTFE cell. Anode gas was separated by a skirt made of each metal or PTFE from hydrogen evolved at a cathode. The cell bottom was insulated by PTFE sheet to avoid mixture of anode gas with hydrogen formed on the bottom due to the corrosion of metal during shutdown. The anode gas was treated with sodium fluoride (NaF) to eliminate HF. Its sample gas was fractionated by means of gas chromatography, and analyzed by infrared spectroscopy. The current efficiencies with respect to these constituents were evaluated from the results of gas analysis and overall flow rate of anode gas.

A Ni working electrode of 2 cm$^2$ effective area through a cover of box-type cell made of PTFE (ca. 2 dm$^3$ volume) was separated by a PTFE skirt from a large-area nickel cathode at which electrolytic hydrogen was evolved. Although the electrode potential was measured against the static potential of platinum wire or a new type of the reference electrode immersed in the same molten electrolyte, it was calibrated to the hydrogen potential in V vs. $H_2$. The cell positioned in a chamber filled with dry nitrogen to avoid moisture, and was warmed with a heater to 120°C.

Pre-electrolysis at low current densities with a carbon anode was conducted for many hours until $\text{NF}_3$ was generated and the electrolytic cell was stabilized before the polarization measurement and/or corrosion testing. A nickel working electrode washed with water was rinsed
with methanol to remove trace water prior to weighing. The anode was weighed before and after electrolysis to evaluate weight loss and the corresponding current loss. In this case, the concentration of water in the electrolyte could not be determined, but it might be less than 0.02 wt% (about 21 mmol/dm$^3$) (4).

In experiments with the production cell, the electrolyte of NH$_4$F·
2HF was prepared with highly pure HF (99.99%) and NH$_4$F·HF (purity of 99.7%), but the cell was positioned in the atmosphere. Electrolysis was conducted at 120°C soon after the electrolyte was charged in the cell. However, in our experiments it was not possible to determine the concentration of water in the melt.

**RESULTS AND DISCUSSION**

Fig. 1 illustrates the change of the current efficiencies of NF$_3$-formation (curves 1, 2 and 3) and total anode gas (curves 4, 5 and 6) during electrolysis at 25 mA/cm$^2$ using copper, steel and nickel cells as a function of time, respectively. Using copper cell, the best current efficiencies of NF$_3$-formation (60%) and total anode gas (90%) were obtained. The current efficiency of hydrogen evolved at a cathode was 70-75% in every cell. The current losses caused by the anodic dissolution of nickel in copper cell (3.5%) was larger than those in a steel cell (1.5%) and in a nickel cell (2.5%). The results obtained were given in Table 1 together with that in a steel cell having a nickel skirt.

Fig. 2 shows the change of the concentrations of nickel, iron and copper ions in each cell with a course of time. The concentration of nickel ion was the lowest in a copper cell (0.060 mol%), while it was the highest in a nickel cell (0.100 mol%). In a steel cell, iron ion of 0.010 mol% was also present in addition to the almost same concentration of nickel ion (0.065 mol%) as that in a copper cell. The concentration of copper ion was only 0.001 mol% and copper deposited was observed on the cell bottom in a copper cell.

The effect of metal complex salts such as NH$_4$NiF$_3$ and (NH$_4$)$_3$FeF$_6$ on the current efficiencies of NF$_3$-formation, total anode gas and cathode gas were investigated in a H-type PTFE cell without and with a diaphragm made of PTFE filter, and the results were given in Table 2 and 3, respectively. Electrolysis with a carbon anode was conducted in the same melt, as reference to the result obtained in electrolysis with a nickel anode. When a carbon (FE-5, Toyo Tanso Co. Ltd.) anode was used, the current efficiencies of both total anode gas and hydrogen evolution
reached to about 96% and 97%, respectively. In the PTFE cell without the diaphragm, they were decreased by some 6% when the carbon anode was substituted by a nickel anode. The addition of metal complex salts decreased them by a further 16 to 26%. In contrast, in the PTFE cell with the diaphragm, they were not almost decreased by the addition of some complex salts and using a nickel anode, in comparison with those using a carbon anode. It is therefore concluded that heavy metal impurities, especially Ni and Fe compounds, in the electrolyte are harmful to the production of NF₃.

Fig. 3 shows the effect of the additives and impurities on the current loss caused by the anodic dissolution of nickel (Qₐ/Qₜ, %) during electrolysis at the current density of 25 mA/cm². Open circle (curve 1) and closed circle (curve 2) designate the Qₐ/Qₜ obtained in the electrolyte with and without the treatment of pre-electrolysis for the purpose of elimination of water in the fluoride melt, respectively. In Fig. 3, the nickel anode was prevented from corrosion when a small amount of nickel ions exists in the electrolyte. Also, the value of Qₐ/Qₜ obtained in a well dehydrated melt of NH₄F·2HF was higher than that in molten fluoride containing water. Since it is reported that the solubility of α-NiF₂ is dependent upon the concentration of water in liquid HF (5), the behavior in molten NH₄F·2HF may be caused by the same reason as that in liquid HF.

From these results, it is concluded that nickel ions such as Ni²⁺ and NiF₃⁻ exhibit both the positive and negative behaviors for the process proposed, considered with the effect as described in the current efficiencies for NF₃-formation, total anode gas and hydrogen evolution (see Tables 1, 2 and 3) and that the concentration of nickel ions in molten NH₄F·2HF may be decided by the concentration of water in the electrolyte. Consequently, we estimate the optimum concentration of total nickel ions some 0.06 mol% to keep the current efficiency of NF₃-formation high.

REFERENCES

1) A. Tasaka, K. Miki, T. Ohashi, S. Yamaguchi, M. Kanemura, N. Iwanaga and H. Arimitsuka; Proceedings of The International Symposium on Molten Salt Chemistry and Technology 1993, p. 306 (1993).
2) A. Tasaka, H. Itoh, T. Isogai, H. Aio and T. Tojo; J. Electrochem. Soc., 138, 421 (1991).
3) A. Tasaka, K. Mizuno, A. Kamata and K. Miki; J. Fluorine Chem., 57, 121 (1992).
4) T. Nakajima, T. Ogawa and N. Watanabe; J. Electrochem. Soc., 134, 8 (1987).
5) A. F. Clifford and A. C. Tulumello; J. Chem. Eng. Data, 8, 425 (1963).

Fig. 1 The change of the current efficiencies of N$_3^-$ formation and total anode gas during electrolysis at 25 mA/cm$^2$ using copper, steel and nickel cells as a function of time.

1(C) N$_3$(in Copper cell) 4(●) total anode gas(in Copper cell)
2(Δ) N$_3$(in Iron cell) 5(●) total anode gas(in Iron cell)
3(C) N$_3$(in Nickel cell) 6(●) total anode gas(in Nickel cell)
Table 1  Effects of cell material on both current loss caused by anodic dissolution of nickel ($Q_a/Q_t$) and current efficiencies of each product in anode gas, total anode gas and hydrogen evolution in electrolysis at 25 mA/cm$^2$ and 120°C for 70 hours in molten NH$_4$F-2HF.

| Cell Skirt | Current efficiency of anode, cathode gas products (%) | $Q_a/Q_t$ (%) |
|------------|------------------------------------------------------|---------------|
| Copper     | 58.1, 20.8, 2.33, 3.58, 0.19, 7.33, 92.3, 67.7, 3.53 |               |
| Iron       | 44.9, 13.6, 5.47, 2.11, 0.55, 5.96, 72.5, 73.6, 1.46 |               |
| Nickel     | 40.4, 28.5, 2.70, 4.15, 0.15, 5.65, 82.4, 77.5, 2.65 |               |
| Iron       | 44.6, 24.6, 3.53, 3.82, 0.36, 5.19, 82.1, 82.9, 2.02 |               |

Fig. 2  The change of the concentrations of nickel, iron and copper ions in each cell with a course of time.

1(○): Nickel ion(copper cell)  4(●): Copper ion(copper cell)  
2(△): Nickel ion(iron cell)  5(△): Iron ion(iron cell)  
3(■): Nickel ion(nickel cell)  4(●): Iron ion(nickel cell)  
5(△): Iron ion(iron cell)
Table 2  Effects of NH$_4$NiF$_3$ and (NH$_4$)$_3$FeF$_6$ added in molten NH$_4$F·2HF on both current loss caused by anodic dissolution of nickel ($Q_a/Q_t$) and current efficiencies of each product in anode gas, total anode gas and hydrogen evolution in electrolysis at 25 mA/cm$^2$ and 120°C in a PTFE cell without a diaphragm.

| Anode material | Additive (mol%) | Current efficiencies of anode and cathode gas (%) | $Q_a/Q_t$ (%) |
|----------------|----------------|--------------------------------------------------|---------------|
| Carbon         |                | $\text{N}_2 \quad \text{O}_2 \quad \text{N}_2\text{F}_4 \quad \text{N}_2\text{F}_2 \quad \text{N}_2\text{O}$ |               |
| Nickel         |                | 35.3 52.0 5.00 0.47 1.30 1.58 95.7 97.1 - |
| Nickel        | NH$_4$NiF$_3$ 0976 | 31.4 45.2 4.13 0.59 2.69 5.83 89.8 90.9 3.24 |
| Nickel        | (NH$_4$)$_3$FeF$_6$ 0933 | 24.2 38.1 3.81 0.73 1.79 1.48 70.1 74.0 2.60 |

Table 3  Effects of NH$_4$NiF$_3$ and (NH$_4$)$_3$FeF$_6$ added in molten NH$_4$F·2HF on both current loss caused by anodic dissolution of nickel ($Q_a/Q_t$) and current efficiencies of each product in anode gas, total anode gas and hydrogen evolution in electrolysis at 25 mA/cm$^2$ and 120°C in a PTFE cell with the diaphragm made of PTFE filter.

| Anode material | Additive (mol%) | Current efficiencies of anode and cathode gas (%) | $Q_a/Q_t$ (%) |
|----------------|----------------|--------------------------------------------------|---------------|
| Nickel         | NH$_4$NiF$_3$ 0976 | 31.2 54.1 3.58 1.06 1.91 1.41 93.3 94.9 2.34 |
| Nickel        | (NH$_4$)$_3$FeF$_6$ 0933 | 29.3 53.4 4.76 0.76 1.92 2.24 92.4 94.5 2.11 |

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Fig. 3 Relationship between current loss caused by anodic dissolution of nickel ($Q_a/Q_t$) and the concentration of $\text{NH}_4\text{NiF}_3$. 

1 (o); In a well dehydrated melt of $\text{NH}_4\text{F} \cdot 2\text{HF}$, 
2 (●); In molten $\text{NH}_4\text{F} \cdot 2\text{HF}$ containing water.