ELECTROLYTIC PRODUCTION OF NITROGEN TRIFLUORIDE WITH A NICKEL BASED COMPOSITE ELECTRODE PREPARED BY HIP

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ABSTRACT

The nickel-based composite materials prepared by HIP and a nickel sheet were employed as the anode for electrolytic production of NF3. The mixed gas composed of NF3 and N2 with a small amount of N2F2, N2F4, N2O, and O2 was liberated at the Ni sheet and every nickel based composite anodes during electrolysis at 25 or 50 mA/cm2. The current efficiency for NF3 formation on the Ni-5 mol% Co3O4 composite anode (40.99%) was small compared with that on the Ni sheet anode, while its anode consumption (11.6%) was much larger than that of the Ni sheet anode. The current efficiency for NF3 formation on the Ni-Mn02 composite anode was also small and its anode consumption was very small compared with those of the Ni sheet and the Ni-Co3O4 composite anodes, because of the anode surface coated with the dense oxidized layer with few pores. The current loss caused by anodic dissolution of Ni-10 mol% MnO2 composite (0.81%) was small compared with that of Ni-5 mol% MnO2 composite (1.74%). On the other hand, the current efficiency for NF3 formation on the Ni-NiO composite anode electrolyzed in a molten NH4F ⋅ 2HF (ca. 53%) was almost the same or small compared with that of the Ni sheet anode, and the addition of LiF in a molten NH4F ⋅ 2HF increased it. The anode consumption of the Ni-NiO composite anode was small compared with that of the Ni sheet anode. The oxygen content in the oxidized layer formed on the Ni-NiO composite anode was high compared with that on the Ni sheet anode.

From these results, it is concluded that the Ni-NiO composite anode is more favorable for electrolytic production of NF3 and that the oxidized layer on the Ni-NiO...
A large amount of nitrogen trifluoride (NF$_3$) is consumed as a dry etchant and a cleaner gas for the CVD chamber by the electronic industry in Japan. Pure NF$_3$ free from carbon tetrafluoride (CF$_4$) can be obtained by the electrolysis of NH$_4$F·2HF with a nickel anode to meet demand. However, relatively large corrosion rate and passivation of the nickel anode are problems for electrochemical production of NF$_3$. According to the previous works (1 to 3), the nickel dissolution is diminished by a trace of water in the melt whereas the current efficiency for NF$_3$ formation is decreased. The surface layer on the anode formed in a molten salt containing water was tight and its oxygen content was high (2, 3). When the oxidized layer on the nickel anode has the higher content of nickel oxide, it has the electric conductivity and the higher resistance to corrosion (4). It is known that the highly oxidized nickel fluorides such as $\beta$-NiF$_3$, $\rho$-NiF$_3$, and NiF$_5^-$ play an important role in the electrochemical fluorination processes at the nickel anode in a molten NH$_4$F-HF system and the other systems (5). Also, the highly oxidized cobalt fluoride and manganese fluoride such as CoF$_3$ and MnF$_3$ are used as a fluorinating agent for synthesizing some organic compounds. Hence, the nickel-oxide composites such as Ni-NiO, Ni-Co$_3$O$_4$, and Ni-MnO$_2$ systems were prepared by HIP from the mixture of each oxide and Ni powders.

This paper deals with the effect of the content and the kind of oxide material in the composite on the current efficiency for NF$_3$ formation and the anode consumption.

**EXPERIMENTAL**

The mixtures of metal oxides such as Co$_3$O$_4$, MnO$_2$ (purity of 99.9%) and NiO (purity of 97.0%, particle size of 1 $\mu$m) and Ni (purity of 99.9%, particle size of 2.9 to 3.6 $\mu$m) powders were sintered at 900°C under 2000 atm for 2 hours by Hot Isotactic Pressing (HIP). The ratio of oxide in the mixture was 2, 5, and 10 mol%. These samples were used as the Ni-oxide composite electrode, and the anodic behaviors of them were investigated in a dehydrated melt of NH$_4$F·2HF at 100°C.

A box-type PTFE cell of ca. 0.5 dm$^3$ was provided for electrochemical and corrosion studies, and the cell configuration was described in the previous paper (1, 3.
4) The composite specimen and the nickel sheet having a large surface area were used as the anode and the cathode, respectively. A nickel rod immersed in molten NH$_4$F·2HF saturated with NH$_4$NiF$_3$ was used as the reference electrode and the potential was calibrated to the potential of hydrogen evolution using another box-type PTFE cell. The construction of the reference electrode was also illustrated in the previous paper (2). The potential of the reference electrode was measured in a molten NH$_4$F·2HF at 100 °C and its value was 93 ± 5 mV. When the electrochemical measurement, the corrosion test, and the preparation of the specimen for the XPS analysis were conducted, the PTFE cell was positioned in a dry box. Since the chemicals contained water to some extent, pre-electrolysis was conducted with a carbon anode at ca. 10 mA/cm$^2$ for about ten days to reduce the water content to less than 0.02 wt% (6, 7) or ca. 20 millimoles per dm$^3$ prior to the electrochemical, corrosion, and XPS studies. For the corrosion test, the nickel anode was washed with water and methanol before weighing. The current losses caused by nickel dissolution with an assumption of two-electron transfer for the reaction [1]:

$$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e$$

[1]

were calculated from the weight loss.

The cell employed for electrolytic production of NF$_3$ was cylindrical Ni cell (1.5 dm$^3$) as described in the previous paper (1, 8). The Ni and the composite sheets of 19.2 cm$^2$ in surface area were employed as the anode. The anode located at the center of cell whereas the cell wall was utilized as the cathode. 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 and the loss of NF$_3$ are prevented. The cell bottom was covered with the PTFE sheet to avoid hydrogen evolution.

Electrolysis was conducted 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% within 80 hours (9). The anode gas was treated with NaF to eliminate HF before the chromatographic and IR spectroscopic analyses (1). The current efficiencies for the constituents were evaluated from the results of gas analysis and the flow rate of anode gas (1, 5, 9).

In order to prepare the specimen for SEM, XPS, and XRD studies, the nickel anode was electrolyzed at 25 or 50 mA/cm$^2$ in a dehydrated melt of NH$_4$F·2HF at 100°C for 100 to 150 hours. The test specimen was washed with 47% HF aqueous solution to remove adhesive melt on the surface prior to inspection by XPS, XRD, and SEM. ESCA-1000 (Shimadzu Seisakusho Ltd.) with Al-K$_x$ radiation (1400 eV) was used for the XPS analysis (1 to 5, 9).
RESULTS AND DISCUSSION

1. Preparation of Ni-NiO, Ni-CoO, and Ni-MnO_2 Composite Materials by HIP

A nickel sample was at first prepared by HIP from a nickel powder. The density of HIPed nickel was 8.8763 g/cm³, and was almost the same as that of the commercial nickel sheet (purity of 99.6%, Nilaco Corporation Co. Ltd.). Hence, it is found that the material prepared by HIP is dense and has a small porosity.

The Ni-CoO and the Ni-MnO composite materials were prepared at 900°C under 2000 atm for 2 hours from the mixture of CoO or MnO and a Ni powder as a binder. Figures 1 and 2 show the XRD patterns of the Ni-5 mol% CoO and the Ni-10 mol% MnO composites prepared, respectively. The composites were composed of cobalt oxide (CoO) or manganese oxide (MnO) and nickel with a small amount of nickel oxide formed according to reactions [2] and [3], respectively.

\[
\begin{align*}
\text{Ni} + \text{Co}_3\text{O}_4 &\rightarrow \text{NiO} + 3\text{CoO} \quad [2] \\
\text{Ni} + \text{MnO}_2 &\rightarrow \text{NiO} + \text{MnO} \quad [3]
\end{align*}
\]

The Ni-NiO composite material was also prepared from the mixture of NiO and Ni powders under the same conditions by HIP. The XRD patterns indicated that the composite prepared by HIP was composed of NiO and Ni.

2. Anodic polarization curves

The anodic polarization curves of the specimens were determined in a dehydrated melt of NH_4F·2HF at 100°C by the potential sweep method with a sweep rate of 100 mV/s. Figure 3 is the anodic polarization curve of the Ni-CoO composite, and figure 4 is that of the Ni-MnO composite. A virgin Ni-CoO composite anode has a current peak at ca. 0.2 V due to Ni dissolution and passivated in the range of 1 V to 2 V. A new current peak appeared at ca. 2.7 V presumably due to the reoxidation of cobalt oxide, CoO, and oxygen evolution reaction according to reactions [4] and [5].

\[
\begin{align*}
3\text{CoO} + \text{H}_2\text{O} &\rightarrow \text{Co}_3\text{O}_4 + 2\text{H}^+ + 2e \quad [4] \\
2\text{H}_2\text{O} &\rightarrow \text{O}_2 + 4\text{H}^+ + 4e \quad [5]
\end{align*}
\]

The current density increased with sweeping potential from ca. 3.3 V to 4 V, probably caused by fluorination of nickel and cobalt oxides, and reached a plateau in the potential range between 5 V and 6 V due to the oxidation of nickel (II) to nickel (III) and/or (IV) compounds. Electrochemical fluorination may occur at the potentials higher than 5 V (3, 10).
The potential sweep measurement with the same specimen was repeated in the potential range of 0 V to ca. 9 V. Curve 2 is a trace of the second run, which differs from curve 1. The peak and the following plateau caused by active dissolution at ca. 0.2 V to 0.5 V disappeared because of the formation of the protective layer composed of nickel fluoride with nickel oxide or oxifluoride at potentials higher than 5 V during the first run. No current passed in the potential range of 0.5 V to 2 V. Thereafter, the similar behavior of current to that of curve 1 was observed with sweeping potential, but the amperage was small compared with that observed in curve 1. Curve 3 represents the 50th run and the shape of wave is the same as of the second run whereas the amperage is further small compared with that in curve 2 because of the growth of oxidized layer during repetition of sweeping potential.

Figure 4 shows the anodic polarization curves of the Ni-10 mol% MnO₂ composite. Curves 1, 2, and 3 represent the first, the second, and the 50th runs, respectively. Every shape of wave is similar to that of the Ni-5 mol% Co₃O₄ as shown in Fig. 2. The anodic polarization curves of the Ni-NiO composites were also determined and were almost the same as of the Ni-Co₃O₄ composite (11).

Figure 5 illustrates the chronopotentiograms of the Ni sheet and the Ni-NiO composite anodes. The top figure, labeled (a), is the potential of the Ni sheet anode, and the middle figure, labeled (b), is of the Ni-10 mol% NiO composite anode. Also, the bottom figure, labeled (c), is of the Ni-10 mol% NiO composite anode in a dehydrated melt of NH₄F·2HF containing LiF. The potential of the Ni sheet anode stagnated at 0.2 V for several minutes soon after switch-on, acutely jumped to 6.2 V and then changed through two maxima and two minima to become constant followed by extensive fluctuation in the potential range between 5.0 V and 5.6 V. On the other hand, the potential of the Ni-10 mol% NiO composite anode also stagnated at 0.2 V for several minutes soon after switch-on, and it moved to the second level at 3.2 V prior to the final level at ca. 5 V. The steady state potentials of the specimens at ca. 5.3 V or 5.0 V were fluctuated, presumably caused by repetitive electrochemical formation and dissolution of surface oxide on the Ni substrate. When the melt of NH₄F·2HF contains LiF, the potential behavior of the Ni-10 mol% NiO composite anode is similar to that in the NH₄F·2HF melt without LiF, and the final potential is ca. 5.3 V. The duration of stagnation at 3.2 V increased with the content of NiO in the Ni-NiO composite, and the anode gas evolved at this potential was composed of N₂, O₂, and N₂O without fluorine-containing compound. The electrochemical fluorination of NH₄⁺ took place at 5 V.

3. **Surface Morphologies of the Nickel-Oxide Composite after Electrolysis**

Figure 6(a), 6(b), and 6(c) illustrates the SEM profiles of the Ni sheet and the
Ni-oxide composite anodes after electrolysis at 50 mA/cm$^2$ for 100 hours. The specimens were taken out of the melt under a steady state when the potential became constant. The top-left photograph, labeled (a), is of the surface of the oxidized layer formed on the Ni sheet, and the top-right photograph (b), is of the oxidized layer formed on the Ni-5 mol% Co$_3$O$_4$ composite anode. The middle-left photograph, labeled (c), is of the oxidized layer formed on the Ni-10 mol% MnO$_2$ composite anode. The surface of the Ni sheet specimen was vigorously corroded to be rough as shown in Fig. 5(a). That of the Ni-5 mol% Co$_3$O$_4$ composite specimen was also rough. In contrast, the Ni-10 mol% MnO$_2$ composite specimen had a tight surface with few traces of crevices.

Figure 6(d), 6(e), and 6(f) also illustrates the SEM profiles of the Ni sheet, the Ni-5 mol% NiO composite, and the Ni-10 mol% NiO composite anodes after electrolysis at 25 mA/cm$^2$ for 120 hours. The procedure for preparation of the specimen was the same as described above. The middle-right, the bottom-left, and the bottom-right photographs, labeled (d), (e), and (f), are the surfaces of the oxidized layers formed on the Ni sheet, the Ni-5 mol% NiO composite, and the Ni-10 mol% composite anodes, respectively. The Ni-NiO composite specimens have the dense and tight surfaces of the oxidized layer containing the higher oxygen content.

4. Electrolysis of a Molten NH$_4$F-2HF with the Ni-Co$_3$O$_4$, the Ni-MnO$_2$, and the Ni-NiO Composite Anodes

Electrolysis of NH$_4$F-2HF with and without LiF was conducted at 50 mA/cm$^2$ with the Ni-Co$_3$O$_4$ (5 mol%) composite and the Ni-MnO$_2$ (5 and 10 mol%) composite anodes and at 25 mA/cm$^2$ with the Ni-NiO (2, 5, and 10 mol%) composite anodes. Temperature of the electrolyte was kept constant at 100°C during experiments. In these cases, the anode gas was composed of N$_2$, O$_2$, NF$_3$, N$_2$F$_2$, N$_2$F$_4$, and N$_2$O, and was the same as that in electrolysis of the same melt with the Ni sheet anode. Table 1 shows the current efficiencies for the constituents in the anode gas, the overall generation of anode gas, and hydrogen evolved at the cathode, and the current loss caused by Ni dissolution. Electrolysis with an anode of commercial Ni sheet was conducted as a control. The current efficiency for NF$_3$ formation on the Ni-5 mol% Co$_3$O$_4$ composite anode was 41.0%, and it was small compared with that on the Ni sheet anode. However, its current loss caused by Ni dissolution was 11.6% and the anode consumption was much larger than that of the Ni sheet anode.

The current efficiency for NF$_3$ formation on the Ni-MnO$_2$ composite anode was 36.8% to 43.6% and was smaller than that of the Ni sheet anode. Also, its anode consumption was very small compared with those of the Ni sheet and the Ni-Co$_3$O$_4$ composite anodes, because of the anode surface coated with the dense oxidized layer.
with few pores. That is, the current losses caused by anodic dissolution of the Ni-5 mol% MnO$_2$ and the Ni-10 mol% MnO$_2$ composites were 1.74% and 0.81%, respectively, and the latter was small compared with the former.

On the other hand, the current efficiency for NF$_3$ formation on the Ni-NiO composite anode electrolyzed in a molten NH$_4$F·2HF was 49.5% to 52.8%, and it was almost the same as or somewhat small compared with that of the Ni sheet anode. The addition of LiF in a molten NH$_4$F·2HF increased the current efficiency for NF$_3$ formation. The anode consumption of the Ni-NiO composite anode was 0.093% to 0.503% and was small compared with the Ni sheet anode. The oxygen content in the oxidized layer formed on the Ni-NiO composite anode was high compared with that on the Ni sheet anode. In the Ni-NiO system, the Ni-5 mol% NiO composite material was the best for both the current efficiency for NF$_3$ formation and the resistance to corrosion.

From these results, it is concluded that the Ni-NiO composite anode is more favorable for electrolytic production of NF$_3$ and that the oxidized layer formed on the Ni-NiO composite anode has the high resistance to corrosion, because of the dense film containing the higher content of oxygen on the anode.

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Table 1  Current efficiencies for the constituents of anode gas and the overall anode gas, and the current loss caused by Ni dissolution $(Q_j/Q_i)$ on the Ni based composite anodes electrolyzed at 25 or 50 mA·cm$^{-2}$ for 100 to 130 hours in a molten NH$_4$F·2HF with and without LiF at 100°C.

| Anode area | Current efficiency of anode gases / % | Current loss caused by Ni dissolution $(Q_j/Q_i)$ / % |
|------------|-------------------------------------|---------------------------------------------------|
| Ni sheet   | $100\text{h}$ | 13.47 | 12.14 | 62.34 | 0.47 | 2.87 | 3.08 | 94.36 | 3.22 |
| Ni sheet   | $100\text{h}$ | 16.07 | 9.85  | 51.78 | 1.01 | 2.37 | 4.63 | 85.70 | 2.31 |
| HIPed Ni   | $120\text{h}$ | 32.67 | 3.98  | 39.99 | 0.60 | 13.84 | 1.93 | 89.66 | 1.68 |
| Ni-5mol%Co$_3$O$_4$ composite | $120\text{h}$ | 10.71 | 2.65  | 40.99 | 9.09 | 7.06 | 1.65 | 72.17 | 11.60 |
| Ni-5mol%Mn$_2$O$_4$ composite | $100\text{h}$ | 16.63 | 9.81  | 43.59 | 0.19 | 0.06 | 3.26 | 33.54 | 1.74 |
| Ni-10mol%Mn$_2$O$_4$ composite | $120\text{h}$ | 19.93 | 9.57  | 36.79 | 2.56 | 0.81 | 0.69 | 70.35 | 0.81 |
| Ni-2mol%MnO$_3$ composite | $100\text{h}$ | 25.98 | 15.69 | 49.48 | 0.73 | 0.77 | 1.17 | 93.81 | 0.45 |
| Ni-5mol%MnO$_3$ composite | $150\text{h}$ | 17.96 | 15.73 | 52.80 | 0.50 | 0.78 | 2.06 | 89.82 | 0.093 |
| Ni-5mol%MnO$_3$ composite+LiF | $130\text{h}$ | 14.94 | 12.97 | 53.85 | 1.04 | 0.74 | 9.11 | 92.67 | 0.263 |
| Ni-10mol%MnO$_3$ composite | $120\text{h}$ | 3.75 | 13.33 | 50.34 | 4.52 | 6.45 | 13.48 | 91.87 | 0.503 |
| Ni-10mol%MnO$_3$ composite+LiF | $120\text{h}$ | 12.26 | 8.34  | 53.79 | 5.89 | 0.95 | 13.28 | 94.51 | 0.279 |

Anode area = 19.2 cm$^2$

Fig. 1  XRD patterns of the Ni-5 mol% Co$_3$O$_4$ composite electrode prepared by HIP.

- : Ni,  □ : NiO,  ■ : CoO.
Fig. 2  XRD patterns of the Ni-10 mol% MnO₂ composite electrode prepared by HIP.

- : Ni, □ : NiO, ■ : MnO.

Fig. 3  Anodic polarization curves of the Ni-5 mol% Co₃O₄ composite electrode in a molten NH₄F·2HF at 100°C by potential sweep method with a sweep rate of 100 mV·s⁻¹.

Curve 1: First run, Curve 2: Second run, Curve 3: 50th run.
Fig. 4 Anodic polarization curves of the Ni-10 mol% MnO\(_2\) composite electrode in a molten NH\(_4\)F·2HF at 100°C by potential sweep method with a sweep rate of 100 mV·s\(^{-1}\).

Curve 1: First run, Curve 2: Second run, Curve 3: 50\(^{th}\) run.

Fig. 5 Chronopotentiograms of the Ni sheet and the Ni-10 mol% NiO composite anodes during electrolysis at 25 mA·cm\(^{-2}\) in a molten NH\(_4\)F·2HF with and without LiF at 100°C.

(a) Ni sheet anode electrolyzed in a molten NH\(_4\)F·2HF,
(b) Ni-10 mol% NiO composite anode electrolyzed in a molten NH\(_4\)F·2HF,
(c) Ni-10 mol% NiO composite anode electrolyzed in a molten NH\(_4\)F·2HF + 0.9 mol% LiF.
Fig. 6 SEM images of the Ni sheet, the Ni-5 mol% Co$_3$O$_4$ composite, the Ni-10 mol% MnO$_2$ composite, the Ni-5 mol% NiO composite, and the Ni-10 mol% NiO composite anodes electrolyzed at 25 mA·cm$^{-2}$ for 100 hours (a, b, c) or at (a) Ni sheet, (b) Ni-5 mol% Co$_3$O$_4$ composite, (c) Ni-10 mol% MnO$_2$ composite, (d) Ni sheet, (e) Ni-5 mol% NiO composite, (f) Ni-10 mol% NiO composite.