DEVELOPMENT OF ANODE FOR ELECTROLYSIS OF (CH₃)₄NF-4HF
ROOM-TEMPERATURE MOLTEN FLUORIDE

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ABSTRACT

The sol-gel LiNiO₂ coated Ni and the sol-gel LaNiO₃ coated Ni sheet anodes were developed to improve the Ni sheet anode for electrolytic synthesis of perfluorotrimethylamine, (CF₃)₃N, using the (CH₃)₄NF-4HF melt as the electrolyte. The LiNiO₂ and the LaNiO₃ films may give the electric conductivity to the Ni sheet anode during electrolysis of the (CH₃)₄NF-4HF melt. (CF₃)₃N was successfully obtained at a ratio of about 25% together with other partially fluorinated gaseous products.

INTRODUCTION

Perfluoroalkyl group, -CF₃, promotes lipophilicity of organic compounds, and therefore perfluorotrimethylamine, (CF₃)₃N, is an important fluorine source for synthesis of useful organic fluorocompounds as medicines and agricultural chemicals, because it easily decomposes to release CF₃ radicals. In addition, Fukaya et al. reported that (CF₃)₃N is a potential fire suppression gas by ab initio calculation (1). This compound has been obtained by electrolysis of trimethylamine, (CH₃)₃N, dissolved in anhydrous HF using Ni anode (2-4). However, the temperature of the electrolyte should be kept below 0 °C during electrolysis, because of a high vapor pressure of HF (ca. 50.6 kPa at 0 °C).

A room-temperature molten fluoride, (CH₃)₄N₄HF melt (3.5 < m < 5.0), is expected to be a useful electrolyte for electrochemical fluorination (5). (CF₃)₃N can be synthesized by electrochemical perfluorination of (CH₃)₄N⁺ cation in the melt, and hence it will be a new process that can replace the Simons process. However, a preliminary study revealed that Ni electrode cannot be used as an anode in pure (CH₃)₄NF-4HF melt for a long time, because a poorly conductive film composed of NiF₂, NiO and/or oxyfluoride is formed on the anode during electrolysis (6). To develop a new electrolytic process using the (CH₃)₄NF-4HF melt in an industrial scale, it is important to improve the performance of the Ni sheet anode by covering with the film having a higher electric conductivity and a lower overvoltage for fluoride ion discharge.

It has been reported that the nickel based composite containing nickel oxide with the plural oxidation states gave a high electronic conductivity to the film formed on the anode.
during electrolysis and decreased the anode overvoltage in the (CH$_3$)$_4$NF·mHF melt (7). LiNiO$_2$ and LaNiO$_3$ are considered to be useful film materials that are stable in the (CH$_3$)$_4$NF·mHF melt.

In the present study, LiNiO$_2$ coated Ni and LaNiO$_3$ coated Ni sheets were prepared by the sol-gel coating method, and their anodic behaviors in the (CH$_3$)$_4$NF·4HF melt were investigated in detail. In addition, the LiNiO$_2$ coated Ni and the LaNiO$_3$ coated Ni sheets were applied to anodes in electrolytic production of (CF$_3$)$_3$N in the (CH$_3$)$_4$NF·4HF melt.

EXPERIMENTAL

Preparation of LiNiO$_2$ coated Ni sheet

LiNiO$_2$ coated Ni sheets were prepared by sol-gel coating method. In the sol-gel coating method, the sol solution was prepared from i-C$_3$H$_7$OLi (99.7%, Aldrich), PVP (M$_w$ = 55000, Aldrich), CH$_3$COOH (99.7%, Wako), and i-C$_3$H$_7$OH (Wako) with molar ratios of i-C$_3$H$_7$OLi : PVP : CH$_3$COOH : i-C$_3$H$_7$OH = 1 : 1 : 10 : 20. The molar ratio of PVP represents the amount of PVP monomer units. The addition of PVP was employed as a polymer binder with Li$^+$ cation in the sol solution (8). The sol solution was dip-coated on the Ni sheet (99.7%, Nilaco), and was converted to a gel film by heating at 200°C for 20 minutes. The dip-coating and heating at 200°C were performed 1, 3, or 5 times. After these coating processes, the gel film was heat-treated at 700°C for 2 hours in air (9). The samples prepared by sol-gel coating method are referred to hereafter as “sol-gel LiNiO$_2$ coated Ni sheets”.

Preparation of LaNiO$_3$ coated Ni sheet

LaNiO$_3$ coated Ni sheets were also prepared by sol-gel coating method. In the sol-gel coating method, the sol solution was prepared from La(CH$_3$COO)$_3$·1.5H$_2$O (99.5%, Wako), PVP, CH$_3$COOH, and i-C$_3$H$_7$OH with molar ratios of La(CH$_3$COO)$_3$·1.5H$_2$O : PVP : CH$_3$COOH : i-C$_3$H$_7$OH = 1 : 1 : 10 : 20. The sol solution was dip-coated on the Ni sheet, and was converted to a gel film by heating at 200°C for 20 minutes. The dip-coating and heating at 200°C were performed 3, 5, or 7 times. After these coating processes, the gel film was heat-treated at 750°C for 2 hours in air. The samples are referred to hereafter as “sol-gel LaNiO$_3$ coated Ni sheets”.

Electrolysis of (CH$_3$)$_4$NF·4HF melt

A room temperature molten fluoride of (CH$_3$)$_4$NF·4HF (Morita Chemical Industries) was used as an electrolyte. Electrochemical measurements and electrolysis were conducted in a three-electrode cell (volume: 200 dm$^3$) shown in Figure 1. The cell and the cap were made of tetrafluoroethylene-perfluoroalkylvinyl ether copolymer (PFA) and polytetrafluoroethylene (PTFE), respectively. The reference electrode was an Ag/Ag$^+$ electrode (0.342 V vs. H$_2$) of which internal solution was 0.01 M AgClO$_4$ + 0.1 M (C$_2$H$_5$)$_4$NBF$_4$ dissolved in CH$_3$CN. For electrochemical measurements, small anodes (10 × 10 mm, both faces) were used. The anodic behavior of the LiNiO$_2$ coated Ni and the LaNiO$_3$ coated Ni sheets were studied by means of linear sweep voltammetry. The
potential was swept from the rest potential to 7 V vs. Ag/Ag⁺ with an automatic polarization system (Hokuto Denko, HZ-3000). Electrolysis of the melt was carried out galvanostatically at 20 mA cm⁻² for 100 hours at room temperature using larger anodes (15 × 20 mm, both faces) and a potentiogalvanostat (Hokuto Denko, HA-303). Anode gas was analyzed by gas chromatography/mass spectroscopy (GCMS-QP2010, SHIMADZU) and gas chromatography (GC-14B, SHIMADZU) equipped with a PORAPLOT Q column (Carrier gas: He) after gaseous HF and F₂ were removed by passing through a tube filled with NaF-pellets and alumina balls. The anodes after electrolysis were washed with CH₃CN and then analyzed by XRD and SEM.

Figure 1. Schematic illustration of an electrolytic cell

![Figure 1. Schematic illustration of an electrolytic cell](image)

Figure 2. X-ray diffraction patterns of (a) the sol-gel LiNiO₂ coated Ni sheet and (b) the sol-gel LaNiO₃ coated Ni sheet prepared by five times of dip-coating process. (○) LiNiO₂, (●) Li₂CO₃, (△) LaNiO₃, (▲) La₂O₃, (□) Ni, and (■) NiO.

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Characterization of sol-gel LiNiO$_2$ coated Ni and sol-gel LaNiO$_3$ coated Ni sheets

X-ray diffraction patterns of the samples are shown in Figure 2. The Bragg peaks from the Ni sheet substrate appeared at 44.5, 51.8, 76.4, 92.9, and 98.4° for all samples. The XRD analysis revealed that LiNiO$_2$ formed on the Ni substrate with NiO and Li$_2$CO$_3$, and also that LaNiO$_3$ formed on the Ni substrate with NiO and La$_2$O$_3$. The cross-sectional SEM images of the sol-gel LiNiO$_2$ coated Ni and the sol-gel LaNiO$_3$ coated Ni sheets are shown in Figure 3-1 and 3-2, respectively. The film thicknesses estimated from those images increased monotonously with an increase of the repetition number of dip-coating. These results suggest that the film thickness is controllable by the sol-gel coating method.

![Figure 3-1. SEM images of the cross-sections of the sol-gel LiNiO$_2$ coated Ni sheet prepared by (a) one, (b) three, and (c) five times of the dip-coating process.](image1)

![Figure 3-2. SEM images of the cross-sections of the sol-gel LaNiO$_3$ coated Ni sheet prepared by (a) three, (b) five, and (c) seven times of the dip-coating process.](image2)

Electrolysis of (CH$_3$)$_4$NF+mHF melt

Figure 4 shows the anodic polarization curves at the pure Ni sheet (c), the sol-gel LiNiO$_2$ coated Ni sheet (a), and the sol-gel LaNiO$_3$ coated Ni sheet (b) in (CH$_3$)$_4$NF·4HF melt at a sweep rate of 10 mV s$^{-1}$. The polarization curve of the pure Ni sheet showed a strong resemblance to that in the NH$_4$F·2HF at 100°C (10). A small current peak due to the anodic dissolution of nickel was observed at ca. 0.2 V, at which the following reactions occurred:

\[ \text{Ni} \rightarrow \text{Ni}^{2+} + 2 \text{e}^- \]  \[1\]

\[ \text{Ni}^{2+} + 2 (\text{FH})_n\text{F}^- \rightleftharpoons \text{NiF}_2 + 2n \text{HF} \]  \[2\]

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Figure 4. Anodic polarization curves of (a) the sol-gel LiNiO₂ coated Ni sheet prepared by five times of the dip-coating process, (b) the sol-gel LaNiO₃ coated Ni sheet prepared by five times of the dip-coating process, and (c) pure Ni sheet in (CH₃)₄NF-4HF melt at a sweep rate of 10 mV s⁻¹ at room temperature.

In the range of ca. 0.5 and 3.0 V, almost no current flowed because of the presence of the passivation film, i.e., NiF₂, formed on the electrode through reactions (1) and (2). At potentials more positive than 3.0 V, the current increased gradually with an increase in potential, where a discharge reaction of (FH)ₙF⁻ anion took place and atomic fluorine, F⁺, was formed according to the following reaction:

(FH)ₙF⁻ → F⁻ + HF + n e⁻ \[3\]

The atomic fluorine generated electrochemically is used for fluorination of organic species in the melt. In contrast, the current peak hardly appeared at ca. 0.2 V on the anodic polarization curve of the sol-gel LiNiO₂ coated Ni and the sol-gel LaNiO₃ coated Ni sheets. This result suggests that the anodic dissolution of Ni was suppressed by the presence of LiNiO₂ and LaNiO₃ films. No current flowed on the sol-gel LiNiO₂ coated Ni and the sol-gel LaNiO₃ coated Ni sheets up to 3.0 V, which is in agreement with the behavior of the pure Ni sheet. The LiNiO₂ and the LaNiO₃ films probably worked as a passivation film like the NiF₂ layer because those films were composed of Ni(III) and Ni(II). The current increased from 3.0 V, and a plateau appeared at ca. 5.0 V. It is speculated that the Ni(II) remained in LiNiO₂ and LaNiO₃ films are oxidized further to electrochemically active Ni(III) and/or Ni(IV) compounds at higher potentials. The current density of the sol-gel LiNiO₂ coated Ni sheet was ca. 650 mA cm⁻² at 7 V and that of the sol-gel LaNiO₃ coated Ni sheet was ca. 300 mA cm⁻² at 7 V. They were much higher than that of the pure Ni sheet. This result indicates that the electric conductivity of the LiNiO₂ and the LaNiO₃ films were much higher than that of the NiF₂ layer formed on the pure Ni sheet.

Electrolysis of the (CH₃)₄NF-4HF melt was conducted with the sol-gel LiNiO₂ coated Ni and the sol-gel LaNiO₃ coated Ni sheet anodes at 20 mA cm⁻² at room temperature to obtain the perfluorinated compound, (CF₃)₃N, as a gaseous-product. Figure 5 shows the variations of the potential of the LiNiO₂ coated Ni sheet anode (a), the LaNiO₃ coated Ni sheet anode (b), and the Ni sheet anode (c) with lapse of time during
electrolysis at 20 mA cm\(^{-2}\) in the (CH\(_3\))\(_4\)NF-4HF melt. The potential on Ni anode rose up to 10 V after electrolysis for only 1 hour, whereas those on the LiNiO\(_2\) coated Ni and the LaNiO\(_3\) coated Ni sheet anodes were kept at 5.04 and 6.54 V after electrolysis for 100 hours, respectively. These results indicate that LiNiO\(_2\) and LaNiO\(_3\) may give the electric conductivity to the Ni sheet anode during electrolysis.

![Figure 5](image)

**Figure 5.** Chronopotentiograms of (a) the sol-gel LiNiO\(_2\) coated Ni sheet anode prepared by five times of the dip-coating process, (b) the sol-gel LaNiO\(_3\) coated Ni sheet prepared by five times of the dip-coating process, and (c) the Ni anode during electrolysis at 20 mA cm\(^{-2}\) in the (CH\(_3\))\(_4\)NF-4HF melt at room temperature.

| Material                  | Anode potential / V vs. Ag/Ag\(^+\) | the composition of evolved gas / % | \(P = (\text{CF}_2\text{H})_2\text{NCF}_3\) and (\(\text{CF}_3\))\(_2\)\(\text{NCF}_2\text{H}\) |
|--------------------------|--------------------------------------|-----------------------------------|----------------------------------|
| (Number of times of the dip coating process) |                                      |                                   |                                  |
| Sol-gel LiNiO\(_2\) coated Ni sheet | 7.01                                  | 66.4                              | 6.7                              | 0.4                              | 5.3                               | 1.9                               | 3.1                               | 19.2                              |
| one time                 | 5.20                                  | 53.9                              | 2.0                              | 5.5                              | 7.3                               | 1.5                               | 8.0                               | 21.8                              |
| three times              | 5.04                                  | 57.1                              | 3.1                              | 0.6                              | 5.8                               | 6.8                               | 1.2                               | 25.4                              |
| five times               | 7.38                                  | 70.4                              | 4.2                              | 5.6                              | 1.8                               | 8.5                               | 3.0                               | 6.8                               |
| Sol-gel LaNiO\(_3\) coated Ni sheet | 6.54                                  | 60.8                              | 3.4                              | 4.7                              | 1.5                               | 8.6                               | 6.0                               | 15.1                              |
| three times              | 6.76                                  | 66.1                              | 4.1                              | 5.8                              | 9.7                               | 2.0                               | 4.8                               | 7.5                               |
| five times               | 7.76                                  | 70.4                              | 4.2                              | 5.6                              | 1.8                               | 8.5                               | 3.0                               | 6.8                               |
| seven times              |                                       |                                   |                                   |                                  |                                  |                                  |                                  |                                  |

The gas evolved at the anode was collected and its composition was analyzed by GC-MS. The anode potentials and the compositions of the anode gas during electrolysis are shown in Table 1. The anode gas was composed of CF\(_4\), NF\(_3\), C\(_2\)F\(_6\), CHF\(_3\), C\(_2\)HF\(_5\), (CF\(_3\))\(_2\)N, CF\(_3\)(CF\(_2\)H), and (CF\(_3\))\(_2\)NCHF\(_2\). The partially fluorinated amines, CF\(_3\)(CF\(_2\)H) and (CF\(_3\))\(_2\)NCHF\(_2\), are described as \(P\) in Table 1, because these two products could not be separated well by GC. The (CH\(_3\))\(_4\)N\(^+\) cation was fluorinated
chemically with atomic fluorine generated electrochemically on the anode to give gaseous perfluorocompounds, CF₄ and (CF₃)₃N (9), according to the following reaction:

\[(\text{CH}_3)_4\text{N}^+\text{F}^- + 24 \cdot \text{F} \rightarrow (\text{CF}_3)_3\text{N} + \text{CF}_4 + 12 \text{HF} \]  

[4]

In this reaction, the hydrogen atoms of the methyl groups in \((\text{CH}_3)_4\text{N}^+\) cation are fluorinated stepwise, because trimethylamine molecules, e.g. \((\text{CH}_2\text{F})_3\text{N}, (\text{CH}_2\text{F})_2\text{NCH}_3,\) and \((\text{CH}_3)_2\text{NCH}_2\text{F},\) having monofluorinated methyl groups, were detected by \(^1\text{H}-\text{NMR}\) measurements (9). In addition, the cleavage of the C-N bond in \((\text{CH}_3)_4\text{N}^+\) cation caused by atomic fluorine produced NF₃, \(\cdot\text{CF}_3, \cdot\text{CHF}_2,\) which resulted in the formation of CF₄, C₂HF₅, NF₃, C₂F₆, CHF₂, and C₂HF₂ as by-products. Figure 6 shows time variation of the composition of the anode gas up to 100 hours when the melt was electrolyzed at 20 mA cm⁻² using the sol-gel LiNiO₂ coated Ni sheet anode prepared by three times of the dip-coating process. The ratio of \((\text{CF}_3)_3\text{N}\) was ca. 50% at 30 minutes, because reaction (4) proceeded mainly. Its ratio decreased to ca. 20% at 30 hours with an increase in the ratio of CF₄, which was caused by the cleavage reaction, and then remained almost constant.

![Figure 6. Time variation of the composition of anode gas evolved at the sol-gel LiNiO₂ coated Ni sheet anode prepared by three times of the dip-coating process at 20 mA cm⁻² in (CH₃)₄NF-4HF melt at room temperature. (●) (CF₃)₃N, (♦)CF₄, (▲) C₂F₆, (●) NF₃, (★) CHF₃, (♦) C₂HF₅, and (×) P[(CF₃)₂NCHF₂ + (CHF₂)₂NCF₃].](image)

The ratio of \((\text{CF}_3)_3\text{N}\) in the anode gas was affected by anode potential in the electrolysis of \((\text{CH}_3)_4\text{NF}-4\text{HF}\) melt with those anodes. For example, the ratio of \((\text{CF}_3)_3\text{N}\) decreased from 25.4 to 19.2% with an increase in anode potential in the region between 5.04 and 7.01 V when electrolysis was carried out with the sol-gel LiNiO₂ coated Ni sheets. The growth of the insulation film, e.g. NiF₂, causes a high anode overvoltage, which leads to an increase in Joule heating at the anode. This Joule heating also enhances the cleavage of C-N bond in \((\text{CH}_3)_4\text{N}^+\) cation, which is caused by atomic fluorine. The maximum ratio of \((\text{CF}_3)_3\text{N}\) of 25.4% was obtained when electrolysis using

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the sol-gel LiNiO₂ coated Ni sheet anode prepared by five times of the dip-coating process was carried out at 20 mA cm⁻² in the (CH₃)₄NF-4HF melt for 100 hours.

The surface morphology of the sol-gel LiNiO₂ coated Ni and the sol-gel LaNiO₃ coated Ni sheets after electrolysis at 20 mA cm⁻² for 100 hours in the (CH₃)₄NF-4HF melt at room temperature was observed by SEM. Figure 7 shows SEM images of the samples before and after electrolysis. The surfaces of those anodes after electrolysis were little rough compared with that before electrolysis and no crack was observed on the surface of those anodes after electrolysis.

Figure 8 shows XRD patterns of the sol-gel LiNiO₂ coated Ni and the sol-gel LaNiO₃ coated Ni sheets electrolyzed at 20 mA cm⁻² for 100 hours in the (CH₃)₄NF-4HF melt at room temperature. The peaks assigned to NiF₂ were observed in addition to the peaks that had been present before electrolysis. Although the following reactions are considered to have occurred on the anode, the presence of the other nickel fluoride compounds was not confirmed by XRD.

\[
\text{LiNiO}_2 + 4 \text{(FH)}_2\text{F}^- \rightarrow \text{NiF}_3 + \text{O}_2 + \text{LiF} + 4n \text{HF} + 4e^- \quad [5]
\]
\[
\text{LaNiO}_3 + 6 \text{(FH)}_2\text{F}^- \rightarrow \text{NiF}_3 + 3/2 \text{O}_2 + \text{LaF}_3 + 6n \text{HF} + 6e^- \quad [6]
\]
\[
\text{LiNiO}_2 + 4 \text{HF} \rightleftharpoons \text{Li}^+ + \text{Ni}^{3+} + 4 \text{F}^- + 2 \text{H}_2\text{O} \quad [7]
\]
\[
\text{LaNiO}_3 + 6 \text{HF} \rightleftharpoons \text{La}^{3+} + \text{Ni}^{3+} + 6 \text{F}^- + 3 \text{H}_2\text{O} \quad [8]
\]
\[
2 \text{NiF}_3 + \text{H}_2\text{O} \rightarrow 2 \text{NiF}_2 + \text{O}_2 + 2 \text{HF} \quad [9]
\]

LiNiO₂ and LaNiO₃ are electrochemically fluorinated to nickel fluorides during electrolysis, resulting in formation of highly oxidized nickel fluoride, lithium fluoride or lanthanum fluoride, and O₂ according to reactions (5) and (6), respectively. Also, LiNiO₂ and LaNiO₃ are dissolved through reaction with HF in the melt to form metal cations such as Li⁺ or La³⁺, and Ni³⁺, fluoride ion and H₂O according to reactions (7) and (8), respectively. A part of highly oxidized nickel fluoride fluorinated water to form O₂, HF, and NiF₂ according to reaction (9). The possibility of these reactions has been reported for the LiNiO₂ coated Ni anode electrolyzed in the NH₄F-2HF melt at 100°C (11). In order to obtain the evidence for the presence of the highly oxidized nickel compound, potential decay curves were determined after electrolysis for 100 hours in the (CH₃)₄NF-4HF melt and shown in Figure 9. The potentials after electrolysis at 20 mA cm⁻² in the (CH₃)₄NF-4HF melt was stagnated at ca. 2.0 V. This fact indicates that the highly oxidized nickel compound was formed on the LiNiO₂ coated Ni and the LaNiO₃ coated Ni sheet anodes in the (CH₃)₄NF-4HF melt and its compound was a powerful oxidizing agent. It is therefore suggested that the highly oxidized nickel compound acts as a fluorinating agent during electrolysis in the same way as the strong fluorinating agents such as NiF₃, K₂NiF₆, Li₂NiF₆, and K₂MnF₆ (12-15). That is, the highly oxidized nickel compound is catalytically active and fluorinates (CH₃)₄N⁺ cation to (CF₃)₃N as a reaction mediator.
Figure 7. SEM images of the cross-sections of the sol-gel LiNiO$_2$ coated Ni sheet prepared by five times of the dip-coating process (a) before electrolysis and (b) after electrolysis, and the sol-gel LaNiO$_3$ coated Ni sheet prepared by five times of dip-coating process electrolyzed (c) before electrolysis and (d) after electrolysis.

Figure 8. X-ray diffraction patterns of (a) the sol-gel LiNiO$_2$ coated Ni sheet prepared by five times of the dip-coating process and (b) the sol-gel LaNiO$_3$ coated Ni sheet prepared by five times of dip-coating process electrolyzed at 20 mA-cm$^{-2}$ for 100 h in (CH$_3$)$_4$NF-4HF melt at room-temperature. ($\varnothing$) LiNiO$_2$, (●) Li$_2$CO$_3$, (△) LaNiO$_3$, (▲) La$_2$O$_3$, (■) Ni, (■) NiO, and (◇) NiF$_2$.

Figure 9. Potential decay curves of (1) the sol-gel LiNiO$_2$ coated Ni sheet anodes prepared by (a) one, (b) three, and (c) five times of the dip-coating process, and (2) the sol-gel LaNiO$_3$ coated Ni sheet anodes prepared by (d) three, (b) five, and (c) seven times of the dip-coating process after electrolysis in the (CH$_3$)$_4$NF-4HF melt at 20 mA-cm$^{-2}$. 

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CONCLUSION

The sol-gel coating method with PVP is a useful technique to prepare the LiNiO₂ and the LaNiO₃ films on the Ni sheet. A new process for electrolytic production of a perfluorinated compound, (CF₃)₃N, using the sol-gel LiNiO₂ coated Ni and the sol-gel LaNiO₃ coated Ni sheets as an electrode in the (CH₃)₄NF·4HF melt at room temperature, was developed. The ratio of (CF₃)₃N in the anode gas was affected by current density and anode potential during electrolysis. A high current density, which forms excess atomic fluorine, and a high anode potential, which lead to an increase in Joule heating, enhanced the cleavage of C-N bond in (CF₃)₃N⁺ cation and then decreased the ratio of (CF₃)₃N in the anode gas. The maximum ratio of (CF₃)₃N (25.4%) was obtained at 20 mA cm⁻² in the (CH₃)₄NF·4HF melt using the sol-gel LiNiO₂ coated Ni sheet.

It is concluded that the anode potential was greatly affected by the content of Ni(III) in the LiNiO₂ and the LaNiO₃ films. The sol-gel LiNiO₂ coated Ni sheet most preferably lowers the anode potential and increases the ratio of (CF₃)₃N.

REFERENCES

1. H. Fukaya, T. Ono, and T. Abe, J. Chem. Soc., Chem. Commun. (1995) 1207.
2. J. H. Simons, US Patent 2616927 (1952).
3. H. Bürger, H. Niepel, G. Pawelke, H. J. Frohn, and P. Sartori, J. Fluorine Chem., 15 (1980) 231.
4. P. Sartori and N. Ignat’ev, J. Fluorine Chem., 87 (1998) 157.
5. K. Mamota, Molten salts, 45 (2002) 42.
6. A. Tasaka, T. Yachi, T. Makino, K. Hamano, T. Kimura, and K. Momota, J. Fluorine Chem., 97 (1999) 253.
7. Yoshio Shodai, Minoru Inaba, Kunitaka Momota, Tomotaka Kimura, and Akimasa Tasaka, Electrochem. Acta, 49 (2004) 2131.
8. Y. H. Rho, K. Kanamura, M. Fujisaki, J. Hamagami, S. Suda, and T. Umegaki, Solid State Ionics, 151 (2002) 151.
9. Y. Shodai, K. Momota, and A. Tasaka, Molten Salt XIII, PV 2002-19, The Electrochemical Society Proceedings Series, Pennington, NJ (2002) 946.
10. A. Tasaka, Y. Tsukuda, S. Yamada, K. Matsushima, A. Kohmura, N. Muramatsu, H. Takebayashi, and T. Mimaki, Electrochim. Acta, 44 (1999) 1761.
11. A. Tasaka, Y. Suzuki, S. Sakaguchi, N. Fukuda, and T. Tojo, Electrochim. Acta, 46 (2001) 4349.
12. P. Sartori and N. Ignat’ev, J. Fluorine Chem., 87 (1998) 157.
13. A. Tasaka, T. Kawagoe, A. Takuwa, and M. Yamanaka, J. Electrochem. Soc., 145 (1998) 1160.
14. A. Tasaka, Y. Suzuki, S. Sakaguchi, N. Fukuda, and T. Tojo, Electrochim. Acta, 46 (2001) 4349.
15. B. Žemva, K. Lutar, L. Chacón, M. F. Beuermann, J. Allman, C. Shen, and N. Bartlett, J. Am. Chem. Soc., 117 (1995) 10025.