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Electrolytic production of NF₃ with a LiNiO₂ coated nickel sheet anode prepared by atmospheric plasma spraying technique

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Abstract

A nickel sheet coated with LiNiO_2 powder having average particle sizes of 40 and 50 µm in diameter by atmospheric plasma spraying technique was employed as the anode for electrolytic production of NF₃. In electrolysis of a molten NH₄F·2HF at 100 °C and 25 mA cm⁻², the anode gas generated at the LiNiO₂ coated Ni sheet anode was composed of N₂, O₂, NF₃, N₂F₂, N₂F₄, and N₂O, and its composition was almost the same as that at the Ni sheet anode. The current efficiency for the NF₃ formation on the LiNiO₂ coated Ni sheet anode was increased to reach the constant value of ca. 55% during electrolysis for 100 h, and it was almost the same as that on the Ni sheet anode. The anode consumption of the LiNiO₂ coated Ni sheet was small compared with that of the Ni sheet. Also, the oxygen content in the oxidized layer formed on the LiNiO₂ coated Ni sheet anode was high compared with that on the Ni sheet anode, and the surface of the LiNiO₂ coated Ni sheet anode was covered with a compact and adhesive film having some defects. Although the bottom of the hollow was covered with a thinner layer, no pore penetrated through the oxidized layer. Hence, the LiNiO₂ coated Ni sheet anode is favorable for the electrolytic production of NF₃, and the oxidized layer on the LiNiO₂ coated Ni sheet anode has the higher resistance to corrosion, because of the compact and adhesive film containing the higher content of oxygen formed on the anode. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nitrogen trifluoride; Nickel oxide coated nickel sheet anode; Atmospheric plasma spraying technique; Current efficiency; Corrosion

1. Introduction

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Large amounts of nitrogen trifluoride (NF₃) is consumed as a dry etchant and a cleaner gas for the CVD chamber by the electronic industry in Japan. Pure NF₃ free from carbon tetrafluoride (CF₄) can be obtained by the electrolysis of NH₄F·2HF with a nickel anode to

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meet demand. However, a relatively high corrosion rate and passivation of the nickel anode are problems for the electrolytic production of NF₃. According to the previous work [1-3], the nickel dissolution is diminished by traces of water in the melt, whereas the current efficiency for NF₃ formation decreases. The surface layer on the anode formed in a molten salt containing water was compact and its oxygen content was high [2,3]. When the oxidized layer on the nickel anode has a higher content of nickel oxide, it has a higher electric conductivity and a higher resistance to corrosion [4]. To elucidate the performance of the Ni sheet anode for the electrolytic production of NF₃ in a molten NH₄F·2HF, the properties of the Ni sheet anode covered with an oxidized layer composed of NiF₂ with a small amount of nickel oxide having multiple oxidation states was investigated with the thermally oxidized and/or fluorinated Ni sheet anode in detail [5]. On the other hand, the addition of LiF in a molten NH4F·2HF increases the current efficiency for NF₃ formation, and also the co-existence of the highly oxidized nickel compounds such as Li₂NiF₆ and NiF₃ in the oxidized layer formed on the Ni anode cause an increase of it [6-8]. Since the nickel oxide coated Ni sheet anode applied for electrochemical fluorination may be compared to a DSA electrode for a brine electrolysis, the LiNiO₂ coated Ni sheet was prepared by atmospheric plasma spraying technique.

This paper deals with the effect of the LiNiO_2 coating on the current efficiency for NF₃ formation and the current loss caused by Ni dissolution.

2. Experiment

A Ni sheet was coated with LiNiO₂ powders (average particle sizes of 40 and 50 μ m) by atmospheric plasma spraying technique, and the specimens were prepared by Tokaro Co. Ltd. The specimens are denoted as the LiNiO₂ (40 μ m) (Specimen B) and the LiNiO₂ (50 μ m) coated Ni sheets (Specimen C), respectively, as shown in Table 1. These samples were used as the anode, and their behaviors were investigated in a dehydrated melt of NH₄F·2HF. The LiNiO₂ (40 μ m) and the LiNiO₂ (50 μ m) coated Ni sheet anodes are also denoted as the anode B and the anode C, respectively, in the text. A fresh nickel sheet (Specimen A) was employed as a control.

A box-type PTFE cell of ca. 0.5 dm³ in volume was provided for the electrochemical and corrosion studies, and the cell configuration was described in the previous paper [1,3,4]. The LiNiO₂ coated Ni sheet specimen (Specimens B and C) of 1 cm² in surface area and a nickel sheet having a large surface area were used as the anode and the cathode, respectively. A nickel rod immersed in molten NH₄F·2HF saturated with NH₄NiF₃ was used as the reference electrode, and the potential was corrected to the potential scale for hydrogen evolution on a Pt plate, designated as V versus H₂, in the text. The potential of this reference electrode determined at 100 °C was 100 ± 5 mV versus H₂ during the electrochemical measurements. 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% [9,10] or ca. 20 mmol dm⁻³, prior to the electrochemical, corrosion, and XPS studies. For the corrosion test, Specimens B and C as well as the Ni sheet anode (Specimen A) were washed with water and methanol before weighing. The current losses caused by nickel dissolution were calculated from the weight loss with the assumption of two-electron transfer for the reaction (1):

$$Ni \rightarrow Ni^{2+} + 2e^{-} \tag{1}$$

The cell employed for the electrolytic production of NF₃ was a cylindrical Ni cell (1.5 dm³) as described in the previous paper [1,11]. Specimens A–C of 19.2 cm² in surface area were employed as the anode. The anode was located at the center of the cell whereas the cell wall was utilized as the cathode. The Ni rod of 0.1 cm² in surface area provided with pre-treatment of anodic oxidation in a dehydrated melt of NH₄F·2HF was used as the reference electrode, and it is considered to function as a Ni/NiF₂ electrode. 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 explosions and the loss of NF₃ are prevented. The cell bottom was covered with a PTFE sheet to avoid hydrogen evolution.

Electrolysis was conducted with the nickel cell at 100 °C. Although the water content was high before startup, it might be decreased by electrolysis to less than 0.02 wt% within 80 h [6]. 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 [1,6,7].

In order to prepare the specimen for SEM, XPS, and XRD studies, the LiNiO₂ coated Ni sheet anode was electrolyzed at 25 mA cm⁻² in a dehydrated melt of NH₄F·2HF at 100 °C for 120 h. 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 Co. Ltd.) with an Al-K_{α} radiation (1400 eV) and RINT-2500 (Rigaku Electric Co. Ltd.) with a Cu-K_{α} radiation were used for the XPS and the XRD analyses, respectively [1–4,6,7].

Current efficiencies for the constituents in the anode gas and the overall anode gas, and the current loss caused by Ni dissolution (Q_a/Q_t) on the Ni sheet and the LiNiO₂ coated Ni sheet anodes electrolyzed at 25 mA cm⁻² in a molten NH₄F·2HF at 100 °C

Specimen	Materials	Current efficiencies of anode gases (%)								Current loss caused by anodic dissolution (Q_a/Q_t) (%)
			N ₂	O ₂	NF ₃	N_2F_2	N_2F_4	N ₂ O	Overall	-
A	Ni sheet	100 h	13.47	12.14	62.34	0.47	2.87	3.08	94.36	3.22
	Ni sheet	100 h	16.07	9.85	51.78	1.01	2.37	4.63	85.70	2.31
В	$LiNiO_2$ (40 µm) coated Ni	100 h	13.11	11.85	55.15	1.21	5.30	7.32	91.94	0.85
	$LiNiO_2$ (40 µm) coated Ni	100 h	25.57	11.88	49.04	0.37	0.22	5.57	87.52	1.29
С	$LiNiO_2$ (50 µm) coated Ni	100 h	19.76	10.96	53.85	2.42	2.18	6.41	95.58	0.85
	$LiNiO_2$ (50 µm) coated Ni	100 h	22.06	10.46	50.41	2.80	3.86	8.78	98.36	1.08
	$LiNiO_2$ (50 µm) coated Ni	100 h	21.00	9.50	56.89	1.50	2.42	3.90	95.21	1.13

Anode area = 19.2 cm^2 .



Fig. 1. XRD patterns of the LiNiO₂ coated Ni sheet prepared by atmospheric plasma spraying technique. (a) LiNiO₂ (40 μ m) coated Ni sheet (Specimen B) and (b) LiNiO₂ (50 μ m) coated Ni sheet (Specimen C): (\bigcirc) Ni; (\square) LiNiO₂; (\blacktriangle) NiO; (\blacksquare) Ni₂O₃.

3. Results and discussion

3.1. The $LiNiO_2$ coated Ni sheet specimen prepared by atmospheric plasma spraying technique

The LiNiO₂ coated Ni sheet specimens (Specimens B and C) were prepared with LiNiO₂ powders having average particle sizes of 40 and 50 μ m by atmospheric plasma spraying technique. Fig. 1 shows the XRD diagrams of the LiNiO₂ coated Ni sheets. The upper figure, labeled (a), is the X-ray diffraction pattern of Specimen B, and the lower figure, labeled (b), is of Specimen C. The XRD analysis indicated that the surface layer of Specimens B and C was composed of

Ni and LiNiO₂ with a small amount of NiO and Ni₂O₃. When a nickel sheet was coated with LiNiO₂ particles by atmospheric plasma spraying technique, a part of LiNiO₂ seemed to be decomposed and/or reduced with a nickel substrate according to reactions (2)–(4), resulting in formation of NiO, Ni₂O₃, and Li₂O [4].

$$2\text{LiNiO}_2 \rightarrow \text{Ni}_2\text{O}_3 + \text{Li}_2\text{O} \tag{2}$$

$$Ni_2O_3 + Ni \rightarrow 3NiO$$
 (3)

$$2\text{LiNiO}_2 + \text{Ni} \rightarrow 3\text{NiO} + \text{Li}_2\text{O}$$
(4)

Fig. 2 illustrates the XPS spectra of Ni $2p_{3/2}$ and O 1s levels on the surface of specimens. The left figure, labeled (1), is the XPS spectra of the surface on Speci-



Fig. 2. XPS spectra of Ni $2p_{3/2}$ and O 1s levels on the LiNiO₂ coated Ni sheet prepared by atmospheric plasma spraying technique. (1) LiNiO₂ (40 µm) coated Ni sheet (Specimen B) and (2) LiNiO₂ (50 µm) coated Ni sheet (Specimen C). (a) Outermost surface. Exposed to Ar⁺ beam with beam current = 20 mA at 2 kV for: (b) 0.5 min; (c) 1 min; (d) 4 min; (e) 20 min.







20 µ m

Fig. 3. SEM images of the LiNiO₂ (40 μ m) coated Ni sheet prepared by atmospheric plasma spraying technique (Specimen B): (a) surface and (b) cross-section.

men B and the right figure, labeled (2), is of that on Specimen C. Curve a is the specimen for the outermost surface while b-e are the data for different exposures, 0.5, 1, 4, and 20 min, respectively. The peaks at 852.7, 854.5, 855.7, and 861.4 eV on the Ni $2p_{3/2}$ spectra are assigned to Ni, NiO, Ni2O3 and LiNiO2, and NiO or Ni₂O₃ and LiNiO₂, respectively [12]. The peak at 852.7 eV on the Ni $2p_{3/2}$ spectrum for the outermost surface was almost not observed (see Fig. 2-1a) or sometimes appeared on the outermost surface (see Fig. 2-2a) and its height was increased with the bombardment time of Ar^+ beam or the depth. This means that the Ni sheet is covered thoroughly with the layer mainly composed of $LiNiO_2$ or that a part of the nickel substrate is exposed, presumably because of the lack of the coverage with LiNiO₂. Also, a large peak at 532 eV on the O 1s spectra is assigned to LiNiO₂ and Ni₂O₃. The results from the XRD and XPS analyses describe that the surface layer of Specimens B and C is composed of LiNiO_2 with a small amount of Ni and nickel oxides such as Ni_2O_3 and NiO.

The surface morphologies of the LiNiO₂ coated Ni sheet were observed by means of SEM. Figs. 3 and 4 show the SEM profiles of Specimens B and C, respectively. The upper figures, labeled (a), are the surfaces of the specimens, and the lower, labeled (b), are the cross-sections of them. Although the LiNiO₂ particles with average diameters of 40 and 50 μ m were used for coating, the particle size on the surface of Specimens B and C is 5–20 μ m. The SEM observation also revealed that the surface of the LiNiO₂ coated Ni sheets (Specimens B and C) prepared by atmospheric plasma spraying technique was rugged and that the thickness of the layers on Specimens B and C was 20–50 μ m.



50 μ **m**



20 µ m

Fig. 4. SEM images of the LiNiO₂ (50 μ m) coated Ni sheet prepared by atmospheric plasma spraying technique (Specimen C): (a) surface and (b) cross-section.



Fig. 5. Chronopotentiograms of the Ni and the LiNiO₂ coated Ni sheet anodes during electrolysis at 25 mA cm⁻² in a molten NH₄F·2HF at 100 °C: (a) Ni sheet (Specimen A); (b) LiNiO₂ (40 μ m) coated Ni sheet (Specimen B); and (c) LiNiO₂ (50 μ m) coated Ni sheet (Specimen C).

3.2. Electrolysis of a molten $NH_4F \cdot 2HF$ with $LiNiO_2$ coated sheet anodes

Fig. 5 illustrates the chronopotentiograms of a fresh nickel, Specimen A, the LiNiO₂ (40 µm), Specimen B, and the LiNiO₂ (50 µm) coated Ni sheets, Specimen C, in a dehydrated melt of NH4F·2HF at 100 °C and 25 mA cm $^{-2}$. The top figure, labeled (a), is the chronopotentiogram of a bare Ni sheet. The middle and the bottom figures, labeled (b) and (c), are of the LiNiO₂ coated Ni sheets, Specimens B and C, respectively. The potential of bare Ni rose up from the static potential at ca. 0.2 to ca. 6.2 V after few minutes of switching, decayed gradually through two maxima and two minima, and tended to a steady state with potential fluctuation between ca. 5.2 and 5.6 V. This behavior is elucidated in the previous paper [5,13]. In the case of the LiNiO₂ coated Ni sheet specimens, the potential jumped to ca. 5.8 V soon after switch-on, decayed gradually, and reached also a steady state with potential fluctuation between ca. 4.6 and 5.2 V. The fluctuation of potential is presumably caused by repetitive electrochemical formation and dissolution of surface oxide and/or fluoride on the Ni substrate [5,13]. The potential at steady state on the coated anode was low compared with that on a bare nickel anode. This fact indicates that the electrical resistance of the surface layer on Specimens B and C is small compared with that on a nickel sheet anode (Specimen A) [4].

Fig. 6 shows an example of the time variation of the current efficiencies for constituents in the anode gas evolved on the anode C. Water in the melt was elec-



Fig. 6. The change of current efficiencies for constituents in the anode gas during electrolysis at 25 mA cm⁻² in a molten NH₄F·2HF at 100 °C with LiNiO₂ (50 μ m) coated Ni sheet electrode (Specimen C) as a function of time: (**I**) N₂; (\triangle) O₂; (**O**) NF₃; (**D**) N₂F₂; (**A**) N₂F₄; (**O**) N₂O.



Fig. 7. XRD patterns of the LiNiO₂ coated Ni sheet anodes electrolyzed at 25 mA cm⁻² for 120 h in a molten NH₄F·2HF at 100 °C: (a) LiNiO₂ (40 μ m) coated Ni sheet (Specimen B) and (b) LiNiO₂ (50 μ m) coated Ni sheet (Specimen C). (\bigcirc) Ni; (\bullet) NiF₂.

trolyzed in preference to the fluorination of NH_4^+ for some 20 h after startup. NF₃ was formed after electrolysis only for 5 h, and the gas composition became constant after electrolysis for 100 h. NF₃ was the main product, followed by N₂ with a small amount of O₂, N₂O, N₂F₂, and N₂F₄.

Under the conditions of interest, NH_4^+ and NH_3 are in equilibrium, as shown in Eqs. (5) and (6),

$$NH_4F + nHF \rightleftharpoons NH_4^+ + F(HF)_n^-$$
(5)

$$NH_4^+ + mHF \rightleftharpoons NH_3 + H(HF)_m^+$$
 (6)

where $F(HF)_n^-$ and $H(HF)_m^+$ are solvated ions of $F^$ and H^+ , respectively, and are now written as F^- and H^+ for simplicity. The amount of NH₃ in the melt is generally considered negligible. Nitrogen trifluoride and nitrogen are evolved at the anode by reactions (7)–(9),

$$NH_4^+ + 7F^- \rightarrow NF_3 + 4HF + 6e^-$$
 (7)

 $2NH_4^+ + 8F^- \to N_2 + 4HF + 6e^-$ (8)

$$2NH_3 \rightarrow N_2 + 6H^+ + 6e^-$$
 (9)

where reaction (9) is the direct discharge of NH_3 adsorbed on the anode. However, the side reactions (10)– (14) may also proceed in parallel to form minor products, e.g. N_2F_2 , N_2F_4 , N_2O , and O_2 ,

$$2NH_4^+ + 10F^- \rightarrow N_2F_2 + 8HF + 8e^-$$
(10)

$$2NH_4^+ + 12F^- \rightarrow N_2F_4 + 8HF + 10e^-$$
(11)

$$2NH_4^+ + H_2O + 10F^- \rightarrow N_2O + 10HF + 8e^-$$
(12)

$$2H_2O + 4F^- \rightarrow O_2 + 4HF + 4e^-$$
 (13)

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (14)

where reaction (14) is the direct discharge of water adsorbed on the anode.

Table 1 shows the current efficiencies for the constituents in the anode gas and the overall current efficiency. The current inefficiency caused by the dissolution of nickel from the anode is shown in the last column. The average current efficiency for NF₃ formation on the anode B, was ca. 53% and that on the anode C (ca. 54%) was similar to that on the anode B. Since the current efficiency for NF₃ formation on a fresh Ni sheet anode was 52-62%, and hence the current efficiency for NF₃ formation on the coated anode was almost the same as that on a bare Ni sheet anode. Although NF₃ is generally detected in the anode gas evolved on a fresh Ni sheet anode after electrolysis for more than 20 h, it is formed on the coated anode after electrolysis for only 5 h, as shown in Fig. 6. The existence of Li⁺ ions on the anode and/or in the melt may cause the higher current efficiency for NF₃ formation, presumably because of deposition of Li₂NiF₆ on the anode, which may act as a strong fluorinating agent [6,8,14,15]. On the other hand, the current loss caused by Ni dissolution on the coated anode (Specimens B and C) was only 0.85–1.29%. Hence, the oxide coating on the Ni sheet anode is effective in decreasing the anode consumption.

3.3. Surface morphologies on the $LiNiO_2$ coated Ni sheet anode after electrolysis of $NH_4F \cdot 2HF$ melt

The surface layer on the coated anodes after electrolysis of NH₄F·2HF melt at 25 mA cm⁻² for 120 h was analyzed by XRD, and the result obtained was shown in Fig. 7. The upper figure, labeled (a), is the X-ray diffraction pattern of Specimen B, and the lower figure, labeled (b), is that of Specimen C. The XRD analysis revealed that the surface layer after electrolysis was composed of NiF₂ and Ni, and no nickel oxide was detected in the surface layer. This means that nickel oxides such as $LiNiO_2$, Ni_2O_3 , and NiO in the layer are dissolved and/or fluorinated during electrolysis to form water and oxygen according to reactions (15)–(20). The formed water is also oxidized to evolve oxygen gas according to reactions (13) and (14).

$$LiNiO_2 + 4HF \rightarrow Li^+ + Ni^{3+} + 4F^- + 2H_2O$$
 (15)

$$Ni_2O_3 + 6HF \rightarrow 2Ni^{3+} + 6F^- + 3H_2O$$
 (16)

$$NiO + 2HF \rightarrow Ni^{2+} + 2F^{-} + H_2O$$
(17)

$$\text{LiNiO}_2 + 4\text{F}^- \rightarrow \text{O}_2 + \text{LiF} + \text{NiF}_3 + 4\text{e}^-$$
(18)

$$2Ni_2O_3 + 12F^- \rightarrow 3O_2 + 4NiF_3 + 12e^-$$
(19)

$$2NiO + 4F^{-} \rightarrow O_2 + 2NiF_2 + 4e^{-}$$
 (20)

Fresh nickel is dissolved during stagnation of potential at 0.2 V as shown in Fig. 5a and then is covered with the oxidized layer mainly composed of NiF₂, resulting in passivity. Even so, the Ni anode is dissolved to some extent to keep passivity by formation of NiF₂ according to reactions (1) and (21), and/or (21').

$$Ni \rightarrow Ni^{2+} + 2e^{-} \tag{1'}$$

 $Ni^{2+} + 2F^{-} \rightleftharpoons NiF_2$ (21)

$$Ni + 2F^- \rightarrow NiF_2 + 2e^- \tag{21'}$$

When a part of the nickel on the coated anode is exposed to a dehydrated melt of $NH_4F\cdot 2HF$ during electrolysis, reactions (1) and (21), and/or (21') also take place on nickel. The oxidized layer may contribute to the stability of passivity, but nickel oxides in the surface layer are dissolved and/or fluorinated by reactions (15)–(20).

Fig. 8 shows the XPS spectra for the anode C after electrolysis of NH₄F·2HF melt at 25 mA cm⁻² for 120 h. The XPS spectra for the anode B is similar to those for the anode C. Curve a shows the features of the outermost surface, and curve e on the bottom is a profile near the Ni substrate. The peak at 852.7 eV on the Ni 2p_{3/2} spectra is assigned to Ni, and the peak height is increased with the bombardment time or the depth. The peaks at 857.7 eV on the Ni 2p_{3/2} spectrum and at 686.0 eV on the F 1s spectrum are assigned to NiF₂ and these peaks diminished with the bombardment time. The peak at 532 eV on the O 1s spectrum appears on the outermost surface (a), and it is assigned to H₂O adsorbed on the surface of the anode. The peaks at 531 and 533 eV near the Ni substrate are assigned to NiO and Ni₂O₃, respectively [5,12,13]. With these results, the oxidized layer on the coated anode after electrolysis is composed of NiF2 with a small amount of NiO and Ni₂O₃, and it is similar to that on a bare nickel after electrolysis.

Fig. 9 shows the depth profiles of the constituents in the surface layer of the test specimens. The ordinate shows the atomic ratio of F/O which is evaluated from the XPS intensities of F 1s and O 1s, and the abscissa is the bombardment time corresponding to the depth. The open triangular and rectangular points are the data for the coated anode (Specimens B and C), respectively, while the open circular points are of a bare Ni sheet anode (Specimen A). The atomic ratio versus time curves for the LiNiO₂ coated specimens electrolyzed at 25 mA cm⁻² resembled to the bare Ni sheet anode electrolyzed at the same current density, whereas the atomic ratios of the former were low compared with that of the latter. This means that the oxygen content in



Fig. 8. XPS spectra of Ni $2p_{3/2}$, F 1s, and O 1s levels on the LiNiO₂ (50 µm) coated Ni sheet anode (Specimen C) electrolyzed at 25 mA cm⁻² for 120 h in a molten NH₄F·2HF at 100 °C. (a) Outermost surface. Exposed to Ar⁺ beam with beam current = 20 mA at 2 kV for: (b) 0.5 min; (c) 1 min; (d) 4 min; (e) 20 min.



Fig. 9. Depth profiles of the oxidized layer on the Ni and the LiNiO₂ coated Ni sheet anodes electrolyzed at 25 mA cm⁻² for 120 h in a molten NH₄F·2HF at 100 °C: (a) Ni sheet (Specimen A); (b) LiNiO₂ (40 μ m) coated Ni sheet (Specimen B); and (c) LiNiO₂ (50 μ m) coated Ni sheet (Specimen C).

the surface layer on Specimens B and C is high compared with that on a bare Ni sheet anode (Specimen A). This may cause the lower electric resistance of the surface layer on Specimens B and C than that on Specimen A, as shown in Fig. 5. Fig. 10 shows the SEM profiles of the surface on a fresh Ni sheet (Specimen A) and the LiNiO₂ (50 μ m) coated Ni sheets (Specimen C) electrolyzed at 25 mA cm⁻² for 120 h in a dehydrated melt of NH₄F·2HF. The left-top figure, labeled (a), is the sur-



Fig. 10. SEM images of the Ni and the LiNiO₂ (50 μ m) coated Ni sheets electrolyzed at 25 mA cm⁻² in a molten NH₄F·2HF at 100 °C: (a) Ni sheet (Specimen A), surface; (b) LiNiO₂ (50 μ m) coated Ni sheet (Specimen C), surface; and (c) LiNiO₂ (50 μ m) coated Ni sheet (Specimen C), cross-section.

face morphology of Specimen A. The lower figures, labeled (b) and (c), are the surface and the cross-section of Specimen C, respectively. The surface of bare nickel sheet anode was rough and had a number of pores (see Fig. 10a). In contrast, the coated anode was covered with the slightly rugged layer, which was compact and adhesive. Also, the SEM image of the cross-section indicates that even the bottom of the hollow is covered with a thinner layer without pores that penetrates through the oxidized layer. This may cause the lower anode consumption during electrolysis.

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