

Development Of Anode For Electrolysis Of $(\text{CH}_3)_4\text{NF}\cdot 4\text{HF}$ Room-Temperature Molten Fluoride

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A room-temperature molten fluoride, $(\text{CH}_3)_4\text{NF}\cdot m\text{HF}$ melt ($3.5 \leq m \leq 5.0$), is expected to be a useful electrolyte for electrochemical fluorination [1]. $(\text{CF}_3)_3\text{N}$ can be synthesized by electrochemical perfluorination of $(\text{CH}_3)_4\text{N}^+$ cation in the melt, and hence it will be a new process that can replace the Simons process, in which trimethylamine, $(\text{CH}_3)_3\text{N}$, dissolved in anhydrous HF is electrolyzed using the Ni anode [2, 3, 4]. However, a previous study revealed that the Ni anode is unfavorable in electrolysis for a long time in the $(\text{CH}_3)_4\text{NF}\cdot 4\text{HF}$ only melt, because an insulating film mainly composed of NiF_2 is formed on the anode during electrolysis [5]. To develop a new electrolytic process using the $(\text{CH}_3)_4\text{NF}\cdot m\text{HF}$ melt in an industrial scale, it is important to improve the Ni sheet anode as that covered with the film having a higher electric conductivity and a lower overvoltage for the fluoride ion discharge reaction.

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 and decreased the anode overvoltage in the $(\text{CH}_3)_4\text{NF}\cdot m\text{HF}$ melt [6]. LiNiO_2 and LaNiO_3 are considered to be useful film materials that are stable in the $(\text{CH}_3)_4\text{NF}\cdot m\text{HF}$ melt. The LiNiO_2 and the LaNiO_3 coated Ni sheet anodes were prepared by a sol-gel coating method. The sol solution was prepared from $i\text{-C}_3\text{H}_7\text{OLi}$ (or $\text{La}(\text{CH}_3\text{COO})_3\cdot 1.5\text{H}_2\text{O}$), polyvinylpyrrolidone (PVP, Mw = 55000), CH_3COOH , and $i\text{-C}_3\text{H}_7\text{OH}$. The sol solution was dip-coated on a Ni sheet, and was converted to a gel film by heating at 200°C for 20 minutes. Dip-coating and heat-treatment at 200°C were alternately performed with several times. After all coating processes, the gel film was heat-treated at 700 or 750°C for 2 hours in air. Fig. 1 shows the X-ray diffraction patterns of the samples. The XRD analysis revealed that LiNiO_2 and LaNiO_3 formed on the Ni substrate with oxides such as NiO and/or La_2O_3 .

Fig. 2 shows the variations of the potential of the Ni sheet anode, the LiNiO_2 coated Ni sheet anode, and the LaNiO_3 coated Ni sheet anode with lapse of time during electrolysis at 20 mA cm^{-2} in the $(\text{CH}_3)_4\text{NF}\cdot 4\text{HF}$ melt. The potential on Ni anode rose up to 10 V for only 1 hour, whereas those on the LiNiO_2 and the LaNiO_3 coated Ni sheet anodes were kept at 6.54 and 5.04 V 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.

The compositions of the evolved gas at the LiNiO_2 and LaNiO_3 coated Ni sheet anodes electrolyzed at 20 mA cm^{-2} for 100 hours in the $(\text{CH}_3)_4\text{NF}\cdot 4\text{HF}$ melt are shown in Table 1. The anode gas was composed of CF_4 , NF_3 , C_2F_6 , CHF_3 , C_2HF_5 , $(\text{CF}_3)_3\text{N}$, $(\text{CF}_2\text{H})_2\text{NCF}_3$, and $(\text{CF}_3)_2\text{NCF}_2\text{H}$. The main constituents in the anode gas were CF_4 and $(\text{CF}_3)_3\text{N}$. The maximum ratio of $(\text{CF}_3)_3\text{N}$ obtained was 25.4% when electrolysis using the sol-gel LiNiO_2 coated Ni sheet anode prepared by the procedure of dip-coating with five times was carried out at 20 mA cm^{-2} in the $(\text{CH}_3)_4\text{NF}\cdot 4\text{HF}$ melt for 100 hours.

These results suggest that the electrolytic production of $(\text{CF}_3)_3\text{N}$ from $(\text{CH}_3)_4\text{NF}\cdot 4\text{HF}$ melt using the LiNiO_2 and

LaNiO_3 coated Ni sheet anodes is a useful process because the electrolytic conductivity of these oxide films on the anode is kept higher during electrolysis.

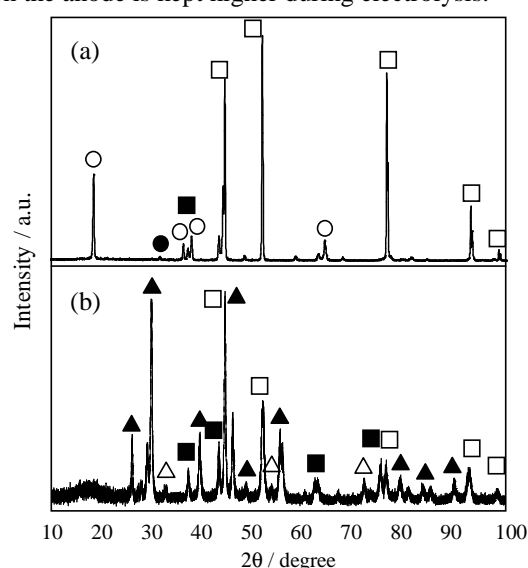


Fig. 1 X-ray diffraction patterns of (a) the sol-gel LiNiO_2 coated Ni sheet and (b) the sol-gel LaNiO_3 coated Ni sheet prepared by the procedure of dip-coating with five times. (○) LiNiO_2 , (●) Li_2CO_3 , (△) LaNiO_3 , (▲) La_2O_3 , (□) Ni, and (■) NiO .

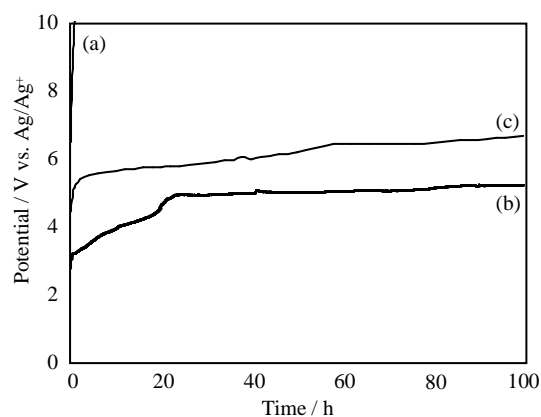


Fig. 2 Chronopotentiograms of (a) the Ni anode, (b) the sol-gel LiNiO_2 coated Ni sheet anode prepared by the procedure of dip-coating with five times, and (c) the sol-gel LaNiO_3 coated Ni sheet prepared by the procedure of dip-coating with five times during electrolysis at 20 mA cm^{-2} in the $(\text{CH}_3)_4\text{NF}\cdot 4\text{HF}$ melt at room temperature.

Table 1 The compositions of the anode gas electrolyzed at 20 mA cm^{-2} for 100 h in the $(\text{CH}_3)_4\text{NF}\cdot 4\text{HF}$ melt at room temperature.

Material (Number of times of the dip coating process)	the composition of evolved gas / %						
	CF_4	NF_3	C_2F_6	CHF_3	C_2HF_5	P	$(\text{CF}_3)_3\text{N}$
Sol-gel LiNiO_2 coated Ni sheet							
three times	53.9	2.0	5.5	7.3	1.5	8.0	21.8
five times	57.1	3.1	0.6	5.8	6.8	1.2	25.4
Sol-gel LaNiO_3 coated Ni sheet							
three times	70.1	4.2	5.6	1.8	8.5	3.0	6.8
five times	60.8	3.4	4.7	1.5	8.6	6.0	15.1

P = $(\text{CF}_2\text{H})_2\text{NCF}_3$ and $(\text{CF}_3)_2\text{NCF}_2\text{H}$

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