Development Of Anode For Electrolysis Of (CH₃)₂NF-4HF
Room-Temperature Molten Fluoride

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A room-temperature molten fluoride, (CH₃)₂NF-mHF melt (3.5 ≤ m ≤ 5.0), is expected to be a useful electrolyte for electrochemical fluorination [1]. (CF₃)N can be synthesized by electrochemical perfluorination of (CH₃)₂N⁺ cation in the melt, and hence it will be a new process that can replace the Simons process, in which trimethylamine, (CH₃)₃N, 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 (CH₃)₂NF-4HF only melt, because an insulating film mainly composed of NiF₂ is formed on the anode during electrolysis [5]. To develop a new electrolytic process using the (CH₃)₂NF-mHF 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 (CH₃)₂NF-mHF melt [6]. LiNiO₂ and LaNiO₃ are considered to be useful film materials that are stable in the (CH₃)₂NF-mHF melt. The LiNiO₂ and the LaNiO₃ coated Ni sheet anodes were prepared by a sol-gel coating method. The sol solution was prepared from La(N(CH₃)₂COO)₃·1.5H₂O, polyvinylpyrrolidone (PVP, Mw = 55000), CH₃COOH, and LiCH₂OH. 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 LiNiO₂ and LiNiO₃ formed on the Ni substrate with oxides such as NiO and/or La₂O₃.

Fig. 2 shows the variations of the potential of the Ni sheet anode, the LiNiO₂ coated Ni sheet anode, and the LaNiO₃ coated Ni sheet anode with lapse of time during electrolysis at 20 mA cm⁻² for 100 hours in the (CH₃)₂NF-4HF melt. The potential on Ni anode rose up to 10 V for only 1 hour, whereas those on the LiNiO₂ and the LaNiO₃ coated Ni sheet anodes were kept at 6.54 and 5.04 V for 100 hours, respectively. These results indicate that LiNiO₂ and LaNiO₃ may give the electric conductivity to the Ni sheet anode during electrolysis.

The compositions of the evolved gas at the LiNiO₂ and LaNiO₃ coated Ni sheet anodes electrolyzed at 20 mA cm⁻² for 100 hours in the (CH₃)₂NF-4HF melt are shown in Table 1. The anode gas was composed of CF₃, NF₃, CF₃NF, CHF₃, CF₂HCF₃, (CF₃)N, (CF₃H)CF₅, and (CF₃H)₂CF₅. The main constituents in the anode gas were CF₃ and (CF₃)N. The maximum ratio of (CF₃)N obtained was 25.4% when electrolysis using the sol-gel LiNiO₂ coated Ni sheet anode prepared by the procedure of dip-coating with five times was carried out at 20 mA cm⁻² in the (CH₃)₂NF-4HF melt for 100 hours. These results suggest that the electrolytic production of (CF₃)N from the (CH₃)₂NF-4HF melt using the LiNiO₂ and

LaNiO₃ coated Ni sheet anodes is a useful process because the electrolytic conductivity of these oxide films on the anode is kept higher during electrolysis.

Reference