Anodic Behavior Of Each Component In A Few Nickel-Metal Composites And Effect Of Added Metal In Composites On Electrolytic Production Of NF_3

Sojiro Kon, Atsuhisa Mimoto, Tsuyoshi Maeda, Minoru Inaba, and Akimasa Tasaka

Department of Applied Chemistry, Graduated School of Engineering, Doshisha University
1-3 Miyako-dani, Tadara, Kyotanabe, Kyoto 610-0321, Japan

Nitrogen trifluoride (NF_3) is mainly used as a cleaner gas and etchant in semiconductor and electronics industries. Pure NF_3 free from CF_4 can be obtained by electrolysis of $NH_4F\cdot 2HF$ melt with nickel anode. However, anode consumption, which corresponds to the current loss of 3-5%, is a problem[1)] to be solved. Also, cobalt and silver fluorides are usually used as a fluorination agent for organic compounds. Hence, the anodic behavior of Co and Ag was studied in a dehydrated melt of $NH_4F\cdot 2HF$, and the Ni-Co and the Ni-Ag composites were employed for the anode in electrolysis of $NH_4F\cdot 2HF$ in order to investigate the effects of each component in the nickel based composites on the current efficiency for NF_3 formation and the anode consumption.

Fig. 1 shows the anodic polarization curves of the Co electrode. Two peaks due to anodic dissolution were observed at *ca*. –0.1 and 0.3 V on the 3rd and the 40th runs. These peaks correspond to Reactions (1) and (2), respectively.

$$Co + 2HF \leftrightarrows CoF_2 + H_2 \qquad E^0 = -0.345\ V\ vs.\ H_2 \quad (1)$$

$$Co + 3HF \leftrightarrows CoF_3 + 3/2H_2 \qquad E^0 = 0.40\ V\ vs.\ H_2 \quad (2)$$

Fig. 2 shows the curves for the Ag electrode. Two anodic dissolution peaks were also observed at *ca*. 1.2 and 1.5 V on the 1st run. These peaks correspond to Reactions (3) and (4), respectively.

$$Ag + HF \leftrightarrows AgF + 1/2H_2 \qquad E^0 = 0.884\ V\ vs.\ H_2 \quad (3)$$

$$Ag + 2HF \leftrightarrows AgF_2 + H_2 \qquad E^0 = ?\ V\ vs.\ H_2 \quad (4)$$

These results revealed that Co and Ag electrodes were covered with a passive film in a molten $NH_4F\cdot 2HF$ during electrolysis.

The mixture of metal (Co or Ag) and Ni powders were sintered at 1000°C under 196 MPa for 2 hours by Hot Isostatic Pressing (HIP). The ratios of metal in the mixture were 5 and 10 mol%. In electrolysis of $NH_4F\cdot 2HF$ at 50 mA cm^{-2} for 120 hours with the Ni anodes such as the Ni sheet and the HIPed Ni, and the Ni-metal composite anodes, the current efficiencies for the constituents in the anode gas and the current loss caused by anodic dissolution (Q_a/Q_t) are shown in Table 1. The current efficiencies for NF_3 formation on the Ni-Co and the Ni-Ag composite anodes were small compared with those on the Ni anodes. The current efficiencies for NF_3 formation were decreased with increasing the contents of metal in the nickel based composite anodes. Also, the current loss caused by anodic dissolution (Q_a/Q_t) on the Ni-Co and the Ni-Ag composites were large compared with those of the Ni anodes. Addition of Co or Ag in the nickel based composite anodes may promote the anodic dissolution. Fig. 3 shows XRD patterns of the Ni-Co and Ni-Ag composite electrodes after electrolysis. The film formed on the Ni-Co was composed of NiF_2 and CoF_2. Also, composition of the film on the Ni-Ag anode was NiF_2 and AgF. Since these metal fluorides are expected to be highly oxidized species such as NiF_3, CoF_3 and AgF_2 during lectrolysis, it is considered that the fluorination ability of CoF_3 and AgF_2 may be small compared with that of NiF_3. In fact, the current efficiency for NF_3 formation on each Ni-metal composite anode was smaller than those of the Ni anodes.

From these results, it is concluded that a nickel electrode containing a lower concentration of impurities such as Co and Ag is more favorable as the anode material for electrolytic production of NF_3.

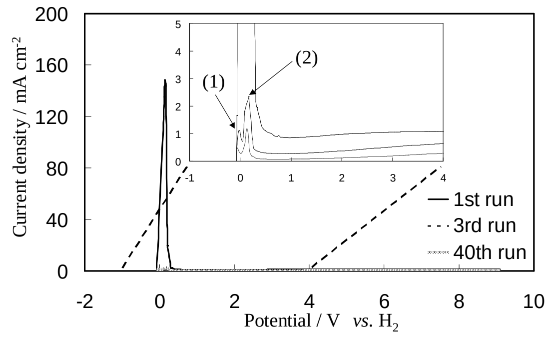

Fig. 1 Anodic polarization curves of the Co electrode in a molten $NH_4F\cdot 2HF$ at 100°C by potential sweep method with a sweep rate of 100 mV s^{-1}.

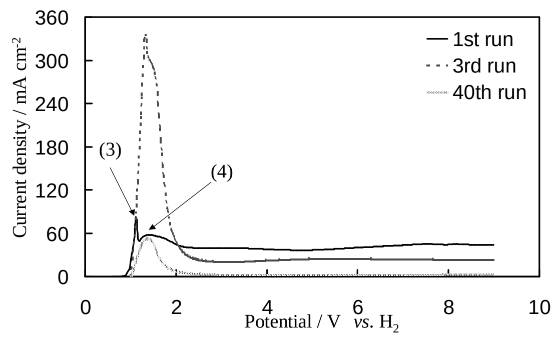

Fig. 2 Anodic polarization curves of the Ag electrode in a molten $NH_4F\cdot 2HF$ at 100°C by potential sweep method with a sweep rate of 100 mV s^{-1}.

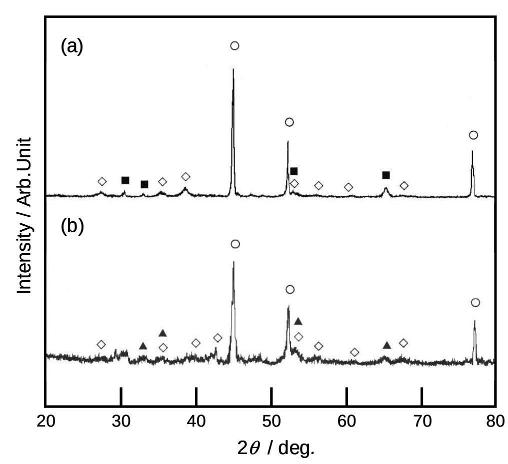

Fig. 3 X-ray diffraction patterns of the Ni-metal composite electrodes electrolyzed at 50 mA cm^{-2} for 120 hours in a molten $NH_4F\cdot 2HF$ at 100°C.

(a) Ni-5 mol % Co composite, (b) Ni-5 mol % Ag composite.

○ : Ni, ◇ : NiF_2, ■ : CoF_2, ▲ : AgF.

Table 1 Current efficiencies for the constituents of anode gas and the overall anode gas, and the current loss caused by anodic dissolution (Q_a/Q_t) on the Ni-metal composite electrodes electrolyzed in a molten $NH_4F\cdot 2HF$ at 100ºC.

Material		Current efficiency of anode gas / %							(Q_a/Q_t) / %
		N_2	O_2	NF_3	N_2F_2	N_2F_4	N_2O	Overall	
Ni sheet	120h	19.18	6.02	**62.84**	1.45	3.03	2.23	94.76	**3.54**
HIPed Ni	120h	14.96	7.71	**60.80**	1.83	2.92	3.69	91.91	**2.18**
Ni-5mol% Co	120h	23.74	8.52	**41.81**	5.96	1.73	3.62	85.39	**7.95**
Ni-10mol% Co	120h	22.08	8.35	**37.60**	7.53	3.32	4.21	83.09	**4.42**
Ni-5mol% Ag	120h	21.16	8.00	**51.71**	2.62	1.19	2.14	86.82	**5.60**
Ni-10mol% Ag	120h	20.40	7.72	**46.77**	4.36	3.44	2.52	85.21	**6.30**

Reference

1) A. Tasaka, T. Ohashi, N. Muramatsu, Y. Nakagawa, and S. Sugimoto, ***Electrochim. Acta*, 45 (2000) 3993.**