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ANODIC BEHAVIOR OF CARBON, GRAPHITE AND NICKEL IN MOLTEN $\text{NH}_4\text{F}\cdot\text{HF}$

Akimasa Tasaka*, Tsukasa Yamamoto, Hideaki Ito and Tetsuro Tojo

Department of Applied Chemistry, Doshisha University, Imadegawa-Karasuma,
Kamigyo-ku, Kyoto 602 (Japan)

The anodic reaction on a carbon, a graphite or a nickel electrode was studied in a molten $\text{NH}_4\text{F}\cdot\text{HF}$ by a few kinds of electrochemical methods. Amorphous carbon, graphite and nickel were used as the anode and Pt-rod as the reference electrode. The anode gas was analyzed by both gaschromatography and infrared spectroscopy.

In the case of carbon anode, the anodic polarization curves obtained by the cyclic voltammetry were divided into four regions with increasing the potential. The current density observed in region I (below ca. 2.4 V) was dependent upon the concentration of NH_4F . In the region II (ca. 2.4 ~ 3.4 V), the current density was also dependent upon the concentration of NH_4F , though the $(\text{C}_x\text{F})_n$ [$x > 2$] film was formed on the surface of carbon. NH_4F was fluorinated in the region III (ca. 3.4 ~ 6.5 V) and then the gas evolved on the anode was composed of $\text{N}_2(+\text{O}_2)$, NF_3 , N_2O , CO_2 , CF_4 and so on. In the region IV (over ca. 6.5 V), the anode effect occurred, but the peak current density at ca. 6.5 V was increased with the number of cyclic scanning. In the case of nickel anode, the anodic current was increased with the number of cyclic scanning, but the cathodic current at the potential below ca. 3.4 V was not observed in this electrolyte, unlike the behavior of nickel anode in liquid HF at 0°C.

From these results, it is suggested as follows: In the case of carbon anode, NH_4F would be directly discharged on the bare carbon and the surface of carbon would be partially restored through the decomposition of $(\text{C}_x\text{F})_n$ and $(\text{CF})_n$ films and their etching with HF in the melt, so that the use of carbon electrode is unfavorable for electrofluorination in this system. In the case of nickel anode, nickel difluoride (NiF_2) formed on the nickel electrode would be dissolved into the melt, and no atomic fluorine adsorbed on the surface of electrode would remain.