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KINETIC STUDY OF CARBON ANODE REACTION IN VARIOUS MOLTEN FLUORIDES

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The electrochemical behavior of carbon electrode in various fluoride melts was studied by different electrochemical methods. Several kinds of carbon material were used as the anode and KF·2HF at 80∿150°C, KF·HF at 260°C, NH_4F·2HF at 50∿120°C and the eutectic mixture of LiF-NaF-KF at 470∿600°C were employed as the electrolytes. Compounds such as $HCOONH_4$, $HCONH_2$, $(NH_2)_2CO$ or NaH_2PO_2 were added into the molten KF·2HF at 80°C. The peak current density at ca. 6 V vs. Pt (i_p) and the minimum current density at potential over 6 V (i_a) were measured from the anodic polarization curves obtained by both the cyclic voltammetry and the potentiostatic method, and then they were interpreted kinetically.

The i_a obtained by the cyclic voltammetry in four melts were dependent upon temperature. From the plots of log i_a against the reciprocal of absolute temperature (1/T), the activation energy of the decomposition of (CF)n film determined in LiF-NaF-KF was 22.0∿25.9 kcal·mol^{-1}. In contrast, that in each case of KF·2HF, KF·HF and NH_4F·2HF was only 5.5∿9.4 kcal·mol^{-1}. The carbon anode was, however, broken in the presence of HF. These results indicate that the disproportionation of (CF)n film is catalyzed by HF and that the physical etching of carbon anode can be explained in terms of formation of an intercalation compound containing HF.

As $HCOONH_4$, $HCONH_2$ and $(NH_2)_2CO$ were added, each additive was adsorbed on the surface of carbon anode. Both $HCOONH_4$ and $HCONH_2$ reduced (CF)n film chemically, while $(NH_2)_2CO$ did not reduce it. However, the addition of $(NH_2)_2CO$ also prevented the formation of (CF)n film by the reaction of adsorbed $(NH_2)_2CO$ with atomic fluorine formed on the anode. In contrast, in the case of NaH_2PO_2, i_a observed on the stationary polarization curve increased with increasing the concentration of the additive, but an acute decrease of current was not observed on the cyclic voltammogram in anodic scan on 30th run even at the lower concentration. This result indicates that the carbon coated by (CF)n film would be also restored through both the physical etching and the chemical reduction of (CF)n film with NaH_2PO_2 in addition to its disproportionation reaction.