S_4

SOME NOVEL GRAPHITE INTERCALATION COMPOUNDS OF FLUORIDES, ELECTRICAL CONDUCTIVITY, AND ELECTROCHEMICAL CHARACTERISTICS AS A CATHODE MATERIAL FOR LITHIUM BATTERIES

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Intercalations of involatile fluorides such as SnF_4 and PbF_4 into graphite have been found in anhydrous liquid HF saturated by fluorine. Detailed X-ray analyses have revealed that the intercalation reaction proceeds through the substitution of bifluoride (HF_2^-) by fluorometallate as follows;

$$C_x + 1/2F_2 + HF \longrightarrow C_x^+HF_2^-, \quad MF_4 + 2HF \longrightarrow MF_5^- + H_2F^+,$$
$$MF_6^- + 2HF \longrightarrow MF_6^{2-} + H_2F^+, \quad C_x^+HF_2^- + MF_y^- \longrightarrow C_xMF_y^- + HF_2^-.$$

Identity periods of C_xSnF_y and C_xPbF_y are, respectively, 11.53 and 11.48 Å. Average thickness of the intercalant are 4.9 Å for both compounds, which indicates the interlayer spacing between graphite layers including intercalants are governed by octahedral hexafluorometallate MF_6^{2-} or bipyramidal pentafluorometallate MF_5^-. Detailed compositional, structural, and physical properties have been investigated on the basis of X-ray analyses, XPS, ^{19}F-NMR, and Mössbauer spectroscopies.

The liquid HF-F_2 system will provide a novel synthetic pathway to graphite intercalation compounds with involatile fluorides. In fact, the GIC of borofluoride (C_xBF_y) has been successfuly prepared in the $LiBF_4$-HF-F_2 solution.

In-plane electrical conductivity of higher stage compounds of C_xSnF_y is 5.4-7.4 times higher than that of pristine HOPG. An attractive feature of of these GIC's is stability in moist air; only a slight change was observed in both X-ray diffraction pattern and conductivity after exposure to moist air over a period of one week.

Electrochemical characteristics of the GIC's as a cathode material for lithium batteries have been investigated by the cells; $Li/1M\text{-}LiClO_4/C_xMF_y$. These cells give very high open circuit voltage ranging from 3.9 to 4.2 V, however the overpotentials are considerably high, and the discharge potentials at 0.1 mA/cm^{-2} are 1.1-2.5 V with cathode utility more than 85%.