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FLUORINE CHEMISTRY AND ELECTROCHEMISTRY – FLUORINE EVOLUTION, GRAPHITE INTERCALATION COMPOUNDS OF FLUORINE AND BATTERY APPLICATIONS

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Our interest in graphite fluorides originated from studies of the phenomenon 'anode effect' in molten fluoride electrolysis for the production of elemental fluorine. Anode effect is the phenomenon that the electrolytic current is suddenly interrupted with increase in cell voltage during the electrolysis of fluoride melt such as KF_2HF . In the course of studies to clarify the origin of the anode effect, it was found that the compound formed on the carbon anode surface during electrolysis was graphite fluoride and that its extremely low surface energy was responsible for this troublesome phenomenon. Since then, interest in this compound has led to the systematic research of the fluorination reaction, structure, and physicochemical properties of carbon material. The addition of metal fluoride such as LiF to electrolyte makes it possible to electrolyze under a higher current density. The role of LiF has not been clear for a long time. Synthesis of fluorine-graphite intercalation compound C_xF in the presence of LiF has revealed that LiF facilitates fluorine intercalation in carbon anode with avoidance of the formation of C-F covalent bond.

Two kinds of graphite fluoride have so far been discovered; $(\text{CF})_n$ and $(\text{C}_2\text{F})_n$. These materials are covalent compounds of graphite; however, they can be regarded as graphite intercalation compounds of stage-1 and stage-2, respectively. $(\text{C}_2\text{F})_n$ can be prepared only from a highly crystallized graphite such as natural graphite by the direct fluorination at rather lower temperature range of 350-400°C. Graphite fluorides consist of an infinite array of trans-linked cyclohexane chairs and are therefore electric insulators. Most characteristic feature in physical properties is low surface energy which is lower than that of polytetrafluoroethylene. The interlayer force between graphite fluoride layers is also very low, which leads to the development of a new solid lubricant.

Graphite fluorides are chemically stable but very active for electrochemical reduction and are excellent cathode materials for lithium batteries with high and stable discharge potential, high energy density and long shelf life under a wide range of temperature. Discharge reaction mechanism has been clarified, and discharge performances are essentially controlled by structural properties.