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NEW SALTS OF GRAPHITE, $C_{12}^{+}HF_2^{-}$ & $C_{24}^{+}SiF_5^{-}$ AND THE THRESHOLD FOR THE OXIDATIVE INTERCALATION OF GRAPHITE

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Third row transition metal hexafluorides (MF_6) for which the electron affinity exceeds 130 kcal/mole (M = Os, Ir, Pt) have been found to intercalate graphite with electron oxidation of the host lattice, whereas those with inferior electron affinities (M = W, Re) do not intercalate[1]. This behavior can be rationalized on kinetic or thermodynamic grounds; arguing for the latter, a simple Born-Haber cycle may be used which suggests an electron affinity threshold of 120-130 kcal/mole for the MF_6 intercalation reaction. For the general case of intercalation reactions by metal fluorides (with or without added fluorine), wherein the graphite lattice is oxidized, the threshold is determined by the free energy of the half-reaction which produces the intercalating fluoro-anion. The lattice energy of the graphite salt must also be taken into account when comparing free energy thresholds for large (e.g., MF_6) and small (e.g. HF_2^{-}) intercalating species.

We have evaluated the free energy of formation of a number of fluoro-anions from the heats of formation and lattice energies of salts which contain them. These studies indicate a threshold free energy of ca. 110 kcal/mole for graphite intercalation. Two 'borderline' second stage compounds, $C_{24}^{+}SiF_5^{-}$ and $C_{12}^{+}HF_2^{-}$, have been synthesized.

1 N. Bartlett, E. M. McCarron, B. W. McQuillan and T. E. Thompson, Synthetic Metals, 1, 221 (1979).

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GRAPHITE INTERCALATION COMPOUNDS OF FLUORINE AND METAL FLUORIDES

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Ternary intercalation compounds of graphite with fluorine and metal fluorides (AlF_3, MgF_2) are prepared under fluorine atmosphere at temperatures of 20-400°C, containing many fluorine atoms chemically adsorbed on the carbon layers and a small amount of metal fluoride. These compounds show a high discharge potential of 2.8-2.5 V vs Li at current densities 40-400 $\mu A/cm^2$ as a cathode material of lithium cell. The electrical conductivity of pyrolytic graphite intercalated by fluorine and magnesium fluoride is higher by one order than that of original sample.