Enhanced thermal stability of semi-covalent graphite fluoride in primary lithium batteries

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Two types of graphite fluoride CF_x have been so far synthesized and used as cathodes in primary lithium batteries; covalent and semi-covalent. The differences between the two lies in the nature of the C-F bonding, being strongly covalent in former, in which C adopts the sp^3 hybridization and semi-covalent in the latter which maintains the sp^2 planar hybridization. Covalent CF_x is prepared at high temperature (450-650ºC), when semi-covalent compound can be obtained at as low as ambient temperature.

The C-F binding energy as measured by XPS shows approximately 1.5-2 eV difference in both C1s and F1s between these materials. As consequence, the discharge voltage of lithium battery based on semi-ionic CF_x is 500-600 mV higher than that based on covalent one. In addition, the rate capability in much higher for the semi-ionic compound due to faster lithium diffusion and higher electrical conductivity.

Commercial Li/ CF_x use covalent-type cathodes. They are among the most thermally stable batteries due to the cathode very high chemical stability towards organic solvent and lithium salts. The discharge products consist mainly of LiF and C which are insoluble.

In this paper, we will present a comparative study on the two types of CF_x regarding their crystal structure, XPS and IR spectroscopy and the cathode performances especially under high discharge rates. A particular emphasis will be put on the thermal stability which is found in the same order in both materials. This is clearly in figure-1 which shows the discharge profile of semi-covalent CF_x after 1 week storage at 60 C. The achieved capacity is 650 mAh/g at 1V. The average discharge voltage is 2.77V under C/10 rate.

Figure-1: Discharge profile of Li/$LiClO_4$-PC/semi-covalent CF_x after thermal storage at 60C for 1 week.