Composition dependence of the physical and electrochemical properties of fluorinated graphite (CF_x 0.33<x<1)

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Graphite fluorides CF_x (0.33<x<1) were obtained by direct fluorination of natural graphite and coke at high temperatures (375-~450ºC). The powders were characterized by XRD, SEM-EDX, TGA and XPS. Their cathode properties were investigated in lithium cells under different galvanostatic discharge rates. The aim is to draw correlations between the physical and electrochemical characteristics of these materials.

The composition 'x' is determined from the weight uptake after fluorination and by the SEM-EDX analysis, which yielded similar results. In graphite based materials as expected, the composition increases with the fluorination temperature (see table 1). The graphite 002 peak is present in the XRD chart up to x=0.52 together with peaks from the fluorinated phase. The later has the strongest peak appear at 2?~10º (Cu, K_α), which may correspond to the 002 peak of stage 2 C_2F compound[1]. In the coke based $CF_{1.08}$ compound obtained in the 400-450ºC temperature range, the strongest peak appears at higher 2? yielding 7.01Å as interlayer spacing in agreement with the literature[1].

Noteworthy is the XPS results that show a linear composition dependence of the C_{1s} and F_{1s} binding energy of the two strongest peaks as depicted in figures 1 and 2. Our finding differs from other published data were no clear trends in the binding energy vs. composition was reported[1-3]. The increase in the binding energy is the signature of increased covalent character of the C-F bonding as the average degree of oxidation of carbon increases.

Rate capability tests were carried out in Li/CF_x cells in $LiBF_4$-PC-DME electrolyte solution. The results were converted into energy/power Ragone plots shown in figure 3. Although the fully fluorinated coke based material yields the highest energy performance at low rates, it is interesting that at higher rates the difference is narrowed. This suggests favorable discharge kinetics in low-fluorine containing materials. A lower binding energy in samples A to D yields lower discharge overpotential and higher electrical conductivity[1]. The paper will discuss correlations between the crystal and electronic structure of the CF_x materials and their thermal and electrochemical properties.

sample	A	B	C	D	E
T (°C)	375	380	390	400	400-450
t (hrs)	17	32	20	80	NA
x	0.33	0.47	0.52	0.63	1.08

Table 1: synthesis condition and composition of the CF_x samples

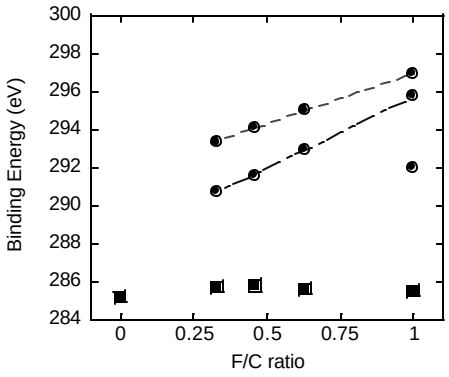

Figure 1: Composition dependence of the C_{1s} electron binding energy in CF_x compounds.

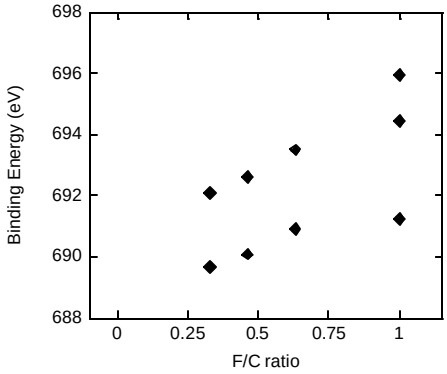

Figure 2: Composition dependence of the F_{1s} electron binding energy in CF_x compounds.

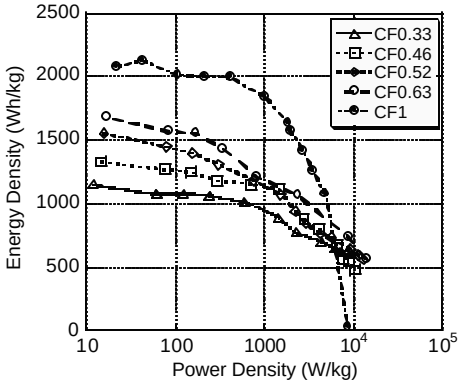

Figure 3: Ragone plot of the Li/CF_x cells

References:
[1] N. Watanabe, T. Nakajima and H. Touhara in Chap. 2, Graphite fluorides, Elsevier 1988
[2] V. N. Mitkin, I. P. Asanov and L. N. Mazalov, J. Struct. Chem. 43(2002)843
[3] G. Nance et al. Carbon 35(1997)175