Fluoride ion electrochemical intercalation into graphitic materials

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Owing to an amphoteric character, graphite can be intercalated by electron donors species such as alkali metals, alkali-earth metals and rare-earth metals and by electron acceptors species such as hydrogen disulphate, nitrates and chlorides [1]. Intercalation can be achieved using chemical and electrochemical means, depending on intercalating species.

In this study we present preliminary results on anodic intercalation of fluoride ions F^- into two types of graphitic materials; synthetic graphite and graphitized carbon multi-walled nanofibers (C-MWNF). Intercalation was carried out in Li/$LiPF_6$-LiF organic solvent/graphitic carbon half-cells.

Schematically F^- intercalation proceeds according to the equation:

$$nC + F^- \rightarrow C_nF + e^- \qquad (1)$$

Figure 1 shows a typical cyclic voltammogram (CV) achieved with C-MWNF in the 3.5-5.3V voltage window. It shows anodic and cathodic peaks corresponding to a step-by-step F^- intercalation and de-intercalation, respectively. Upon further cycling the CV profile did not change much denoting high reversibility of the F^- intercalation and de-intercalation process in C-MWNF. This result contrasts with that obtained with synthetic graphite, which shows poorer cycle life. The differences in behaviour may be ascribed to solvent co-intercalation into graphite due to the open layer structure, a feature less present in C-MWNF. It is known solvent co-intercalation causes expansion of the inter-layers spacing, eventually leading to the layers exfoliation.

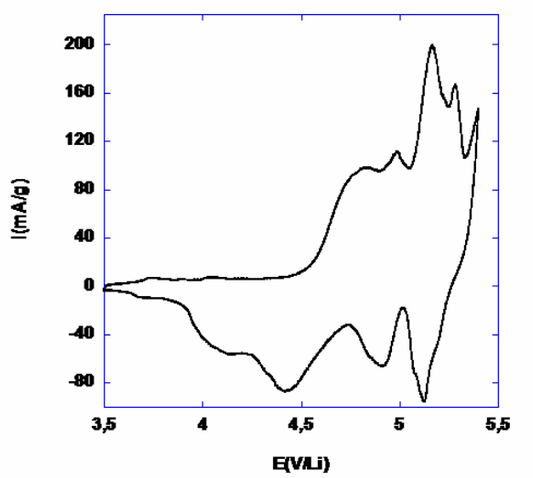

Fig. 1 Typical cyclic voltammogram (0.3mV/s) of F^- intercalation and de-intercalation into C-MWNF

X-ray diffraction was performed on deeply F^- intercalated C-MWNF at 5.3V. Diffraction peaks in Figure 2 fit very well with three phases consisting with intercalation stages of 1, 2 and 3. The stage number refers to the number of grapheme layers between two adjacent intercalated layers. The XRD data displayed in Table 1 are consistent with interlayer spacing (c-parameter) of 4.4 Å, 7.6 Å and 11.2 Å for the stages 1, 2 and 3, respectively.

Nakajima et al. [2] proposed a crystal structure model of chemically intercalated fluorine gas in presence of AgF consisting 'stage-1' type compound with two different interlayer spacing of 4.7 Å and 6.0 Å. In our case a lower interlayer spacing of 4.4 Å suggests F^- anions should be nestled between adjacent carbon hexagons of the graphene layers. The later should then be stacked in the AA sequence. It is our argument that due to strong ionic character of F^- intercalated C-MWNF compound and associated charge transfer to the carbon atoms, fluoride anions should adopt an ellipsoid (flat) shape rather a spherical one, hence reducing their apparent size between the layers. This assumption should be confirmed by independent measurements, however.

The reversible charge-discharge capacity achieved with C-MWNF is about 140mAh/g, which corresponds to $C_{\sim 16}F$ composition at 5.3V vs. Li cut-off voltage.

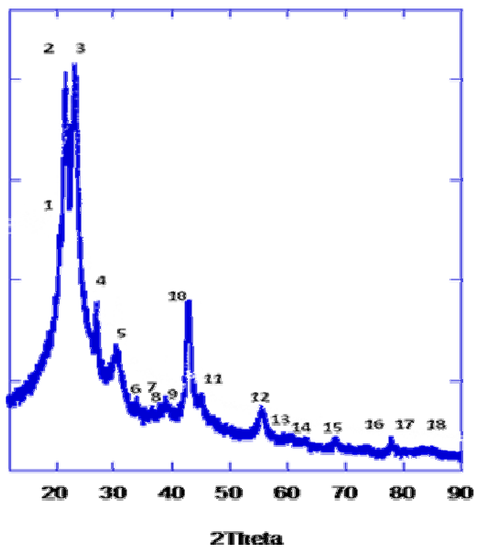

Fig. 2: XRD chart of F^- intercalated C-MWNF at 5.3V vs. Li.

No.	Pos. [2Θ°]	d-spacing [Å]	d-spacing [Å] Calculated Value	Rel. Int. [%]	(hkl)-stage
1	20.3	4.4	4.4	36	CFx(001)-1
2	21.4	4.2	4.2	96	CFx (002)-2
3	22.9	3.9	3.9	100	CFx(003)-3
4	26.7	3.3		18	?
5	30.3	3.0	2.9	17	CFx (004)-3
6	33.7	2.7	2.8	5	CFx(003)-2
7	37.6	2.4	2.3	2	CFx (005)-3
8	38.6	2.3	2.2	6	CFx(002)-1
9	42.5	2.1	2.1	44	CFx (004)-2
10	44.8	2.0	2.0	10	CFx (006)-3
11	55.2	1.7	1.7	9	CFx(007)-3
12	60.4	1.5	1.5	1	CFx (003)-1
13	62.8	1.5	1.5	2	CFx (008)-3
14	68.1	1.4	1.4	4	CFx (006)-2
15	73.4	1.3	1.3	1	CFx(009)-3
16	77.5	1.2	1.2	5	CFx (007)-2
17	84.8	1.1	1.1	1	CFx (004)-1

Table-1: XRD peaks data and indexation of electrochemically intercalated fluoride into C-MWNF at 5.3V

[1] A. Hérold in Chemistry and Physics of Intercalation, Nato Asi series Vol. **72**, 3 (1987)
[2] T. Nakajima et al. Carbon, **29**, 3 (1991)