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X-ray photoelectron spectroscopic study of some pure stages of graphite ferric chloride intercalation compounds

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Abstract

X-ray photoelectron spectroscopic (XPS) study of pure stages 3, 4 and 6 of graphite ferric chloride intercalation compounds (FeCl₃-GICs) have been carried out. The change in the binding energy suggests the nature of charge transfer and lowering of Fermi level as has been reported previously for other acceptor intercalation compounds. The charge transferred/carbon atom is found to reach a maximum for stage 4 and thereafter it remains a constant. \bigcirc 1997 Elsevier Science B.V.

Keywords: Carbon atom; Intercalation compounds; Photoelectron spectroscopy

1. Introduction

Graphite intercalation compounds (GICs) possess diversified properties compared to graphite. GICs are formed by the introduction of atomic or molecular species between the layers of carbon in graphite, which is facilitated mainly by strong intraplanar covalent bonding between the carbon atoms and a weak van der Waals interplanar bonding between the layers. The properties of GICs vary over a range due to the existence of staging (which refers to the number of carbon layers between successive intercalant).

Variations in the properties of graphite on intercalation is mainly due to the interaction between carbon and the intercalant. The charge transfer between carbon and intercalant has been the subject of interest to understand the behaviour of different GICs. Spectroscopic investigations using X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), soft X-ray emission spectroscopy (SXS) [1] and X-ray emission spectroscopy (XES) have contributed to gain insight into the electronic structure of GICs. The charge transfer process in donors has been widely reported in literature [2-5]. Extended X-ray fine absorption structure (EXAFS) has been used to determine the local structure and the chemical identity of intercalated acceptor molecules [6,7]. Mossbauer spectroscopy has been successfully used to obtain information on structural, chemical and charge transfer in systems like antimony [8] halide acceptor intercalates, where in stage-2 SbCl₅ both Sb⁵⁺ and Sb³⁺ intercalant species

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were found and in stage-1 SbCl₅, Sb⁵⁺ is found predominantly. The Sb⁵⁺, Sb³⁺ ratio of intercalant species depended initially on the preparation conditions and was not a direct measure of the intercalation-induced charge transfer. Charge transfer studies from optical reflectance measurements carried out by Amine et al. [9] in Cr and Rb fluoride graphite intercalation compounds have shown the charge transfer coefficients per intercalated species to be f = 0.50 and f = 0.59using Blinowski-Rigaux model [10].

The band structure studies approximate the three dimensional nature of graphite to two dimension, due to the large anisotropy in the bonding between graphite and intercalate. The electronic interaction between the guest and host is a weak interaction, and is controlled by structural details influencing the local geometry of interactions in all three dimensions.

The electronic aspect of intercalation can be approximated to the ionic interactions between graphite and the intercalate, since graphite is amphoteric in nature, i.e. it can accept or donate electrons from/to intercalate and this forms the basis for the formation of both forms of GICs.

The interaction is restricted to graphite π electrons and the σ system of graphite remains unchanged preserving the planar structure of the compound. If there is significant interaction with the σ system, the planar structure is lost and there is a complete loss of metallic nature. The rigidity of graphite layer and the exclusion of significant σ interactions are the reasons for overall weak chemical bonding of the graphite–intercalate complex.

Many investigations have been carried out on donor GICs as mentioned previously and the knowledge on charge transfer in acceptor GICs is very limited. In this communication, we are reporting the nature of charge transfer in the graphite ferric chloride intercalation compound (FeCl₃-GICs) based on XPS investigations carried on some pure stages.

2. Experiment

Highly oriented pyrolytic graphite (HOPG) supplied by Union Carbide, USA, with high 'c'

axis ordering is the parent graphite used and anhydrous ferric chloride supplied by CDH, India is the intercalant. Ferric chloride has a tri-layered structure with iron atoms sandwiched between the chlorine layers and iron is coordinated octahedrally to chlorine atoms [11]. Staged compounds were prepared by the conventional two-zone vapour transport method reported earlier [12]. The reaction is carried out in the presence of chlorine gas at a pressure of 600 Torr. The stages obtained were characterized initially by increase in weight percentage of GIC formed over that of graphite. Accurate stage identification is by X-ray diffraction using CoK α radiation of wavelength $\lambda =$ 1.7902 Å. For a given stage 'n' of $FeCl_3$ -GIC, the (00n+2) peak is of maximum intensity. The 'c' axis repeat distance I_{c} , is related to the stage number by the relation

$$I_c = (n-1) C_0 + d_s$$

where $d_s = d_i + C_0$, is the intercalant sandwich thickness with d_i as the intercalant thickness and C_0 is the interlayer distance in pure graphite. From Bragg's law we have

 $2I_c \sin \theta = l\lambda$

From these two equations, the angle 2θ at which the peak for a given stage should occur can be calculated and the compounds are thus characterized for stages. The 2θ angles at which the (00/) reflections of different stages occur are given in Table 1.

Ta	ble 1							
20	angles	for	the	(00l)	reflections	of	different	stages

(00l) reflections	Diffraction angles 2θ (in degrees)					
	Stage 3	Stage 4	Stage 6			
001	6.38	5.26	3.91			
002	12.78	10.52	7.82			
003	19.23	15.81	11.75			
004	25.73	21.14	15.68			
005	32.32	26.51	19.64			
006		32.00	23.62			
007			27.63			
008			31.67			

Table 2

The C 1s and Cl 2p binding energies and FWHM for HOPG and pure stages 3, 4 and 6 graphite ferric chloride intercalation compound

Compound	Carbon 1s		Chlorine 2p		
	Peak centre eV	FWHM eV	Peak centre eV	FWHM eV	1997 - S. Lancing
HOPG	284.1	1.97			
Stage 3	283.9	1,90	198.6	3.34	
Stage 4	283.6	1.77	197.8	3.06	
Stage 6	283.6	1.76	197.8	2.95	

3. XPS measurement

XPS measurements on freshly cleaved samples were performed using ESCALAB spectrometer with AlK_{α} source operating at 10 kV. The pressure in the analyzer was less than 5×10^{-8} mm. Binding energy scans were carried out for C 1s, Fe 2p and Cl 2p core level regions. Au 4f with binding energy of 83.3 eV was used in calibrating the spectrometer for the binding energy. The binding energies given in Table 2 are the experimentally measured ones and are thus relative to the common Fermi level of the spectrometer and the conductive samples. The depth probed is of the order of 30–50 Å [13].

4. Results and discussions

In a donor GIC, charge is transferred from the intercalant to the graphite. The increased electron density at the carbon atoms should result in a shift to lower binding energy due to better screening of the core charge. This expected shift is compensated for by a shift in the energy scale, due to the change of density of states at the Fermi level. Due to the low density of states in the vicinity of the graphite Fermi energy, the occupation of previously antibonding states by the electrons of guest species, shifts the Fermi edge in the GIC sufficiently closer to the vacuum level [14].

In the acceptor system the C 1s binding energy is shifted to a lower binding energy. Charge is removed from the formerly bonding states below the Fermi energy of graphite. The new Fermi-edge is at lower energies with respect to the vacuum level, and thus the energy scale for photoemission is shifted to lower energies [14].

4.1. C 1s region

The carbon 1s scan spectra for HOPG and stages 3 and 6 are given in Fig. 1. The C 1s electron binding energy measured relative to $E_{\rm F}$ is 284.1 ± 0.2 eV in agreement with that reported in literature [15]. From the data given in Table 2, it is noted that the shift in the C 1s is towards lower binding energy in contradiction with the classical electrostatic rule of increasing energy when decreasing the electronic charge of an atom. Such a contradiction has been observed and reported in LiC₆ donor compound by Rousseau and Estrade–Szwarckopt [16] and for an acceptor by Schlogl [17].

Charge transfer alone does not contribute to the change in binding energy. The final state effects as well as the shift in Fermi level also play a major role in shift of binding energy. For a change in the Fermi level of $\approx 1 \text{eV}$, the charge transferred/atom was shown to be 0.01 e- per carbon atom to the intercalant [18]. In the case of stage 3 compound, in addition to the presence of two graphite bounding layers with which the interactions are confined, there may be interaction with the interior layer present. This can cause the net charge transferred by carbon to be more than that of lower stages. In the case of stage 4, where the interactions with the two interior layers cannot be fully eliminated, the number of carbon atoms available for interaction is greater than that of stage 3. This can be seen from the decrease in binding energy in stage 4 compared with stage 3.



Fig. 1. Carbon 1s spectra of HOPG (----), stage 3 (---) and stage 6 (- - -) graphite ferric chloride intercalation compounds.

The net charge transferred by the carbon atoms is higher in stage 4. As the number of interior layers increases, the interaction of these layers decreases with increasing stage and we observe a saturation effect in stage 6. From the data on full width at half maximum (FWHM) given in Table 2, it is found that it decreases with increasing stage number and then reaches a constant value.

4.2. Chlorine 2p region

The observed binding energy of chlorine 2p in FeCl₃ is 198.8 eV [19]. The change in binding energy in stage 3 as seen from the data given in Table 2 is small revealing the least charge transferred from carbon to FeCl₃. The binding energy change in stage 4 is larger and this is due to greater charge transferred to ferric chloride with contributions from the interior layers and reaches a saturation for stage 6. The values of FWHM of chlorine peaks of various stages are higher than what is expected and this can be due to the existence of C-Cl interactions.

4.3. Iron 2p region

The binding energy of Fe⁺³ state is found to be 710 eV [20]. The binding energy of iron in this GIC is 710 eV confirming the confinement of interactions between carbon and chlorine and iron is affected least by intercalation. This could be due to the tri-layered structure of FeCl₃ where iron is sandwiched between two layers of chlorine.

5. Conclusion

XPS core level spectra of pure stages 3, 4 and 6 graphite ferric chloride intercalation compounds were studied. The binding energy of C 1s is found to shift in opposite direction for ferric chloride intercalated graphite and it cannot be explained by the charge transfer process alone. The binding energy is lower compared to C 1s in HOPG. This is due to lowering of Fermi level in intercalated compound. The FWHM and binding energy tends to reach a saturation behaviour in higher stages due to saturation in the charge transfer/carbon atom even though the number of interior carbon layers increases in higher stages. A similar behaviour is found in Cl 2p spectra and iron is found to be predominantly in +3 oxidation state revealing that interactions are confined to the chlorine atoms in ferric chloride.

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