

STUDIES OF FLUORIDE INTERCALATION IN GRAPHITE ELECTRODES — THE EFFECT OF HF CONCENTRATION ON COMPETITIVE ANODIC PROCESSES

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In 1.0 M and 5.0 M HF solutions, formation of graphite oxide and evolution of O₂ are to be the predominant anodic processes on graphite electrodes. At higher HF concentrations, fluoride intercalation becomes predominant. Polarisation measurements indicate significant reversibility of intercalation/deintercalation processes. Open circuit potential decay and XRD measurements however show some irreversible trapping of fluoride ions. SEM studies also indicate that the surface roughening occurs significantly during the intercalation/deintercalation process.

Keywords: Graphite electrode and hydrofluoric acid

INTRODUCTION

In dilute acidic solutions, graphite electrodes undergo anodic oxidation leading to the formation of surface (phenolic and quinonoid groups) functional groups and irreversible passive phases such as graphite oxides [1,2]. In concentrated acidic media, a reversible anion-intercalation/deintercalation process also occurs [3].



This process has been evaluated extensively in H₂SO₄ media [3-5]. There are relatively fewer studies in other media such as HF media [4,5], though the polarisation behaviour is essentially similar to those in H₂SO₄ media [4,5]. This process could be employed in the operation of a secondary battery [6]. The intercalation behaviour in aqueous and anhydrous HF media were also compared in a brief report [7]. Literature survey thus indicated considerable scope for further efforts in this area.

In this paper, anodic polarisation behaviour of graphite electrode in 1.0 M to 20.0 M HF solutions is reported in detail. The transition from pure surface oxidation process to

intercalation process with acid concentration is traced in steps. In addition to electrochemical measurements SEM as well as XRD methods are used to characterise the initial phases of GIC formation.

EXPERIMENTAL

A 4.7 mm dia high purity commercial graphite (HPCG grade, Graphite India Limited, India) machined and tight-fitted into Teflon was used throughout the study as the working electrode. Polishing and pretreatment procedures described earlier for anodic polarisation studies of glassy carbon electrodes (GCE) in fluoride media [8,9] was employed for activating this electrode as well. The deeply intercalated graphite electrodes usually necessitated polishing for longer periods with rougher emeries.

The electrochemical cells, counter and reference electrodes, electrochemical instrumentation and experimental procedures described earlier for GCE [8,9] were employed as such in the present case as well.

TABLE I: Peak potential and peak currents of redox couples before 1.0 V in CV of HPCG in aqueous HF solutions; $V = 40 \text{ mVs}^{-1}$

No	Parameter	Concn (M)	E_{p1}/i_{p1}		E_{p2}/i_{p2}		E_{p3}/i_{p3}	
			C	A	C	A	C	A
1.	E_p (V)	1	-0.10	0.05	0.54	0.65	—	0.90
2.		5	—	0.06	—	0.35	0.50	0.90
3.		10	—	0.05	—	0.35	0.72	0.85
4.		15	—	0.10	-0.04	0.30	0.60	0.80
5.		20	—	—	—	—	0.70	0.80
6.	i_p (mA/cm ²)	1	0.25	0.25	0.40	1.10	—	0.10
7.		5	—	1.30	—	1.00	0.40	1.00
8.		10	—	2.00	1.00	1.00	3.00	3.20
9.		15	—	1.00	0.80	0.80	3.40	4.20
10.		20	—	—	—	—	4.00	7.40

RESULTS

Voltammetric behaviour in 1.0 M HF solution

Cyclic voltammetric investigations on HPCG in 1.0 M HF show three anodic peaks below 1.0 V anodic limit. All the anodic and cathodic peak currents however increase significantly and become more distinguishable at higher sweep rates. The anodic and cathodic peak potentials and peak current corresponding to the three redox processes obtained at a constant sweep rate of 40 mV/sec are collected and presented in Table I for different HF concentrations.

A significant change in the voltammetric response is noticed once the anodic limit crosses 1.9 V. Typical CV response obtained in 1.0 M HF with the anodic limit of 2.0 V at a sweep rate of 40 mV/sec is presented in Fig. 1A. Whenever

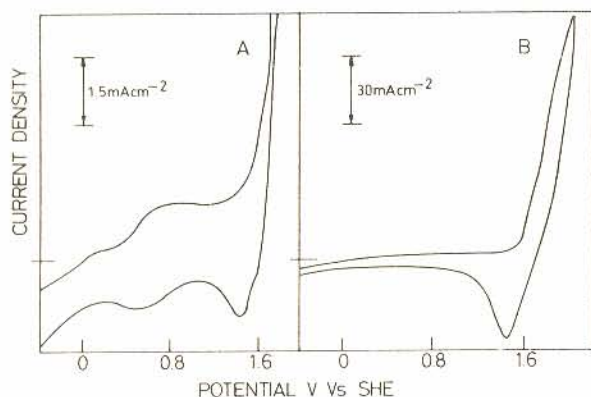


Fig. 1: CV of HPCG in aqueous HF solutions; Concn (M) (A) 1.0 and (B) 5.0; $V = 40 \text{ mVs}^{-1}$

TABLE II: Peak potential and the corresponding peak currents of redox couples after 1 V in CV of HPCG in aqueous HF solutions; $V = 40 \text{ mVs}^{-1}$

Concn M	E_{p4} (V)		E_{p4} mA/cm ²		E_{p5} (V)		E_{p5} mA/cm ²	
	C	A	C	A	C	A	C	A
1	—	—	—	—	1.45	—	1.4	—
5	—	1.75	—	35.00	1.45	1.90	35.0	28.0
10	—	—	—	—	1.38	1.94	40.0	146.0
15	1.28	1.50	54.00	80.00	1.52	1.85	60.0	180.0
20	1.22	1.62	35.00	75.00	1.40	1.82	165.0	175.0

the anodic limit reaches 2.0 V (Table II) a distinct cathodic peak is noticed in the reverse sweep around 1.4 V (Fig. 1A). This cathodic peak current increases with sweep rate as well as with anodic limit reached during the forward sweep. In 0.1 M HF solutions oxygen evolution occurs around 1.6 V and hydrogen evolution occurs around -1.3V.

Effect of HF concentration on voltammetric response

In 5.0 M HF (Fig. 1B) the fifth anodic peak becomes clearly visible around 1.9 V, although it merged with the exponentially increasing background current. Approximate E_p and i_p values for the fourth and fifth peaks are presented in Table II. The O₂ evolution potential lies around 1.8 V and H₂ evolution in this media occurs around -1.0V.

The multisweep CV curves recorded at higher sensitivity clearly show that significant redox processes indeed exist in

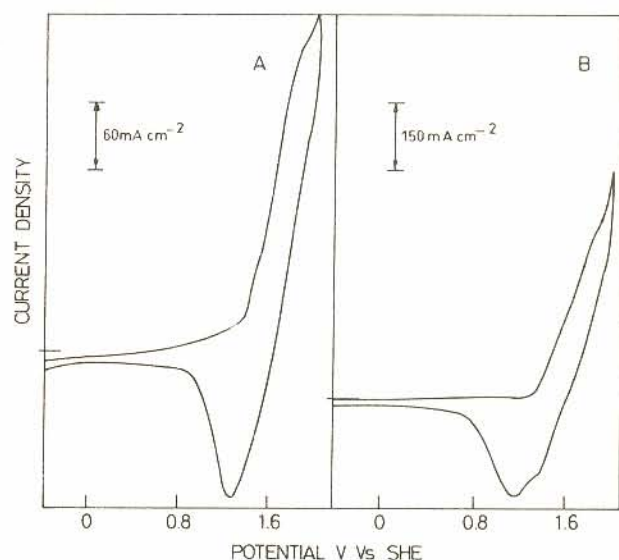


Fig. 2: CV of HPCG in aqueous HF solutions; concn (M) (A) 15 and (B) 20; $V = 40 \text{ mVs}^{-1}$

TABLE III: Intercalation and deintercalation charges and their ratios from CV and i-t transients of HPCG in aqueous HF solutions $V = 40 \text{ mVs}^{-1}$; Anodic limit = 1.8 V

No	Method	Concn (M)	Q_c (mC/cm^2)	Q_a (mC/cm^2)	Q_c/Q_a
1	CV	1	9.0	170.0	0.0529
2		5	288.0	1200.0	0.2395
3		10	890.5	1648.7	0.5401
4		15	850.0	1575.0	0.5396
5		20	2775.0	5475.0	0.5068
6	i-t	1	16.0	192.0	0.833
7		5	154.0	690.0	0.2231
8		10	460.0	977.0	0.4708
9		15	1340.9	2521.7	0.5303
10		20	2146.0	4176.0	0.5138

lower potential region (below 1.0V) as well. The peak currents obtained at different peak potential regions (Table II) increases significantly in 5.0 M HF.

The voltammetric behaviour in 10.0M, 15.0 M and 20.0 M HF solutions are qualitatively quite similar to those discussed above. The CV curves obtained when HPC graphite was polarised upto 2.0 V in 15.0 M and 20.0 M HF are presented in Figs. 2A and 2B respectively. E_{p4} and E_{p5} are more clearly noticed in these figures. In these media, the two closely spaced cathodic peaks are also clearly visible.

The minimum anodic potential limit required for the observation of cathodic deintercalation peak around 1.4 V continues to decrease from 2.0 V in 1.0 M HF to as low as 1.4 V in 20.0 M HF. The O_2 evolution potential also decreases from 1.8 V in 1.0 M HF to 1.5 V in 20.0 M HF. The H_2 evolution potential increases from -1.3 V to -0.64 V under identical conditions.

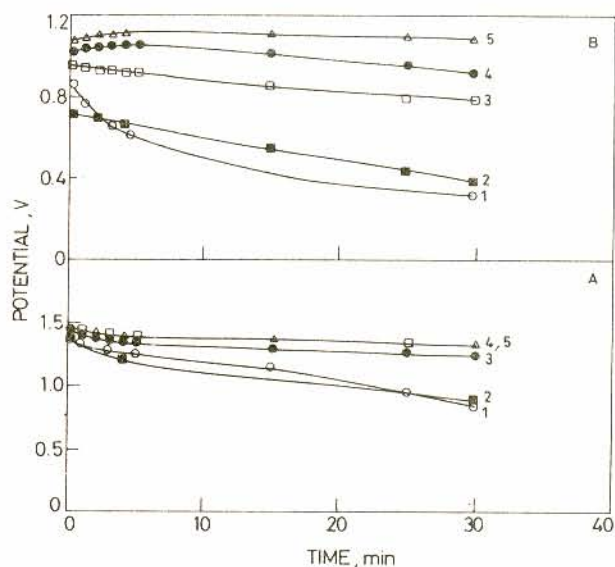
The anodic and cathodic charges (Q_a, Q_c) integrated between 1.0 V and 1.8 V are found to increase significantly with HF concentration. Q_a for example, increases from 170 mC/cm^2 to 2475 mC/cm^2 when HF concentration increases from 1.0 M to 20.0 M. The charge recovery ratio Q_c/Q_a increases from 5% to well beyond 50% with HF concentration. Beyond 15.0 M HF, there appears to be a slight decreases in this parameter (Table III).

To evaluate intercalation/deintercalation efficiencies at constant potential, double potential step chronoamperometric experiments were carried out with an anodic intercalation potential of 1.6 V and a cathodic deintercalation potential

of 1.0 V in 5.0, 10.0, 15.0 and 20.0 M HF aqueous solutions for 60 seconds in each potentials respectively. Both intercalation and deintercalation processes reach a steady state after a sudden initial rise. The steady state intercalation as well as deintercalation currents increase significantly with HF concentration. The Q_a , Q_c and Q_c/Q_a values obtained from these i-t transient measurements are presented in Table III. The similarity in the trend obtained from cyclic voltammetric experiments and i-t transient experiments (Table III) suggests that the intercalation / deintercalation processes noticed in CV experiments above are indeed long - time three dimensional phase changes.

Anodic and cathodic polarisation also result in consistent and steady changes in the open circuit potentials (OCP). Fig. 3A for example shows the OCP decay of graphite in 1,5,10,15 and 20 M HF solutions after anodic intercalation reaction at 1.6 V for 7 minutes in the same solutions. This figure shows that the OCP decays faster in dilute solutions. In concentrated solution the OCP decays much more slowly and remains around 1.4 V even after 30 minutes.

The OCP decay pattern of the same electrodes in the same solutions after deintercalation at 1.0 V for 7 minutes at 1.0 V are presented in Fig. 3B. The OCP once again is found to drop significantly in dilute HF solutions. It is more stable in strong HF solutions. It is indeed quite interesting to note that



*Fig. 3: OCP decay of HPCG after polarisation (A) at 1.6 V and (B) at 1.0 V for 7 minutes in aqueous HF solutions
Concn of HF (M): (1) 1.0, (2) 5.0, (3) 10.0, (4) 15.0 & (5) 20.0*

the graphite deintercalated at 1.0 V in 20.0 M HF solutions show OCP above 1.0V. This is a clear indication that the graphite once intercalated is not totally and reversibly deintercalated in these strong HF solutions.

Microscopic and diffraction studies

The surface transformations during an anodic intercalation/deintercalation for 7 minutes in 15.0 M HF solutions are compared in Fig. 4. Fig. 4A shows the chemical attack of HF on graphite. These attacks, which are noticed only at 3000 times magnification do not enhance further with increasing dip-time beyond 7 minutes as long as no electrochemical polarisation is initiated.

However, significant irreversible surface transformations occur during anodic polarisation and get gradually enhanced with increase in the time of anodic polarisation. Fig. 4B which is obtained after polarising graphite at 1.6 V in 15.0 M HF aqueous for 7 minutes confirms this view. The transformation is further aggravated during cathodic disintegration at 1.0 V as shown in Fig. 4C.

In addition to the signals of fresh graphite sample, a new signal at a 'd' value of 6.529 was noticed in the intercalated sample during XRD measurements. After deintercalation, this signal did not disappear completely.

DISCUSSION

In this middle potential region (below 1.0V) the redox currents on graphite electrodes observed in this work are substantially higher when compared to GCE reported earlier [8,9]. On GCE the current never exceeds 1 mA/cm^{-2} whereas on graphite it can be as high as 10 mA/cm^{-2} . There are only two distinguishable peaks in this potential region on GCE [8,9], whereas three peaks are noted on graphite (Table I). The redox currents on graphite depend markedly on HF concentration (Table I) whereas it is almost concentration-independent on a nonporous compact GCE [8,9]. Graphite surfaces are relatively porous. In addition, even fine emeries used for polishing, create line defects on these graphite material. HF can easily attack this surface sites and oxidise them as indeed noticed in the SEM micrographs (Fig. 4A). This chemical attack is however confined to the graphite surface region alone. Hence the voltammetric response in this region becomes time-independent and reproducible after 5-10 minutes of immersion in the respective acidic media.

In 1.0 M HF solution, even if the electrode is polarised upto 1.8 V, no reversible deintercalation is noticed above 1.0 V

during the reverse sweep on graphite electrode. The anodic peak observed in this medium at about 1.4 V is thus due to graphite oxidation leading to irreversible oxide formation rather than graphite intercalation.

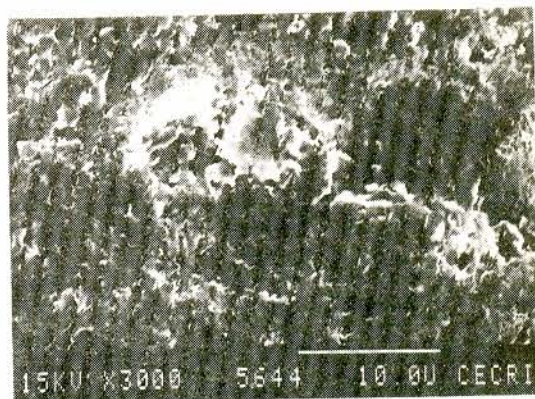


Fig. 4A



Fig. 4B



Fig. 4C

Fig. 4: SEM of HPCG (A) after chemical treatment in 15 M HF aqueous solution for 5 minutes x 3000, (B) after intercalation at 1.6 V for 7 minutes x 100 and (C) after deintercalation at 1.0 V for 7 minutes x 100

On GCE, this type of irreversible surface oxidation is the predominant surface oxidation process upto 2.5 V even in 20.0 M HF solution [8,9]. However, on graphite even in 1.0 M HF reversible graphite intercalation process set-in at about 1.9 to 2.0 V (Fig. 1A). With increasing HF concentration, this intercalation potential shifts to less positive potentials (Table II). However, during anodic sweep, this reaction does not lead to any distinct anodic peak throughout the concentration range. The two poorly defined anodic peaks between 1.0 V to 2.0 V (Table II) are merged with the anodic background current to a very great extent. This implies that the reversible anodic intercalation process always proceeds along with irreversible graphite oxidation and oxygen evolution processes.

The competitive processes of graphite oxidation and oxygen evolution is indeed found to be quite significant in dilute acid solutions. This is clear from very low Q_c/Q_a values from cyclic voltammetric (Table III) as well as potentiostatic polarisation (Fig. 3B) measurements. The minimum potential required for the initiation of intercalation significantly decreases with increase in concentration. The intercalation vs other oxidative processes thus seem to arise from the competition between F^- and H_2O species as the electroactive entity at the electrode surface. The improved intercalation rate with increasing F^- ion concentration also reflects in higher Q_c/Q_a values with HF concentration (Table III).

CONCLUSION

The present investigation on graphite electrode in 1.0 to 20.0 M HF solutions thus indicate a mild chemical attack especially at the active defective surface regions. Fluoride intercalation which is quite low in dilute HF solutions, enhances significantly at higher HF concentrations. The intercalation process always proceeds alongwith fresh surface oxidation and oxygen evolution. During intercalation as well as deintercalation significant irreversible surface structure also occurs. This leads to trapping of certain regions of the graphite intercalation compound. These processes lead to quite low intercalation/deintercalation efficiency.

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