

# Comparison of fluoride intercalation/de-intercalation processes on graphite electrodes in aqueous and aqueous methanolic HF media

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## Abstract

The solvent can play a major role in the intercalation/de-intercalation process and the stability of graphite substrates towards this process. This fact is established in the present work that involves fluoride intercalation/de-intercalation on graphite electrodes in aqueous and aqueous methanolic HF solutions where the HF concentration is varied between 1.0 and 18.0 M. In addition to cyclic voltammetry and potentiostatic polarization, open-circuit potential decay measurements, scanning electron microscopy and X-ray diffraction measurements have been employed. In general, addition of methanol and increasing concentration of HF raise the overall intercalation/de-intercalation efficiency. Methanol is adsorbed preferentially on the graphite lattice and, hence, suppresses both oxygen evolution and the formation of passive graphite oxides. In 15.0 M HF, the optimum methanol concentration is 5 vol.%. This suggests that, in addition to the adsorption effect, there is some weakening of the structured water molecules that facilitates the solvated fluoride ions for efficient intercalation.

*Keywords:* Graphite electrodes; Methanol; Hydrogen fluoride

## 1. Introduction

Solvents can exert a strong influence on the double-layer structure as well as on the electrochemical kinetics at the electrode–electrolyte interface [1,2]. Corresponding effects on the preparation of graphite intercalation compounds (GICs) by chemical means have also received some attention [3–6]. By contrast, solvent effects on electrochemical intercalation/de-intercalation processes have received comparatively little attention.

Because of the relevance to lithium/graphite fluoride batteries, the electrochemical discharge behaviour of chemically prepared graphite fluorides (prepared by the chemical reaction of graphite and fluorine gas at high temperature) has been studied in considerable detail [7–13]. The discharge behaviour of graphite fluorides prepared through the direct fluorination of other GICs [14] and graphite oxides [15] has also been investigated recently. Takanaka et al. [16] have reported briefly on the electrochemical fluorination of graphite in anhydrous HF and 50% aqueous HF media. Beck and Krohn [17] have successfully employed polypropylene-

mixed graphite material to develop a lead/graphite accumulator in aqueous HF solution.

Some preliminary investigations in the authors' laboratory have revealed that, in aqueous HF solutions, commercially available graphite materials undergo irreversible degradation during intercalation/de-intercalation cycles. In aqueous methanolic HF solutions, however, the graphite electrodes are found to exhibit better stability. Detailed evaluation of the fluoride intercalation/de-intercalation processes in these two media is the subject matter of the present work.

## 2. Experimental

The working electrode was made from a rod (diameter = 4.7 mm) of high-purity, commercial graphite (HPCG grade, Graphite India Ltd., India) that was machined and fitted tightly into Teflon. The electrode was activated by using the polishing and pretreatment procedures described previously [18,19] for anodic polarization studies of glassy carbon electrodes (GCE) in fluoride media. When deeply intercalated, the graphite electrodes had to be polished for longer periods with rougher grades of emery paper. AR grade methanol and AR grade 20 M HF were employed for the preparation of aqueous methanolic HF solutions with different concentrations.

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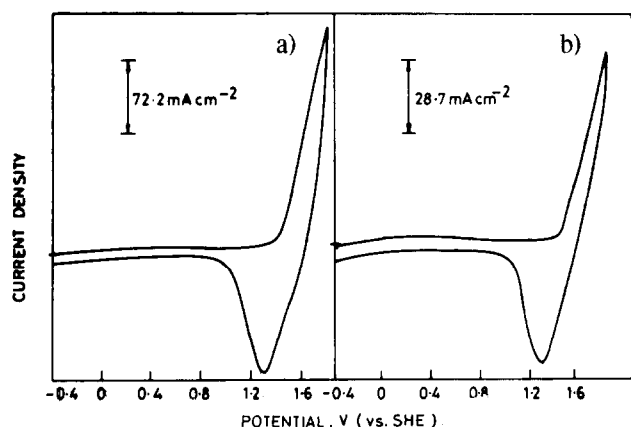


Fig. 1. Cyclic voltammograms for a HPC graphite electrode in 10.0 M HF: (a) aqueous solution, and (b) aqueous methanolic (50 vol.%) solution. Scan rate = 40 mV s<sup>-1</sup>.

Table 1

Intercalation and de-intercalation charges and their ratios from CV of a HPC graphite electrode in aqueous and aqueous methanolic HF solutions

Solution	Concentration (M)	$Q_c$ (mC cm <sup>-2</sup> )	$Q_a$ (mC cm <sup>-2</sup> )	$Q_c/Q_a$
Aqueous	1	9.00	170.00	0.0529
	5	288.00	1200.00	0.2395
	10	890.50	1648.70	0.5401
	15	850.00	1575.00	0.5396
	18	2775.00	5475.00	0.5068
Aqueous methanol	1	4.38	38.27	0.1144
	5	136.90	663.50	0.2063
	10	304.10	675.24	0.4504
	15	1206.80	1824.60	0.6614
	18	1954.94	2701.15	0.7234

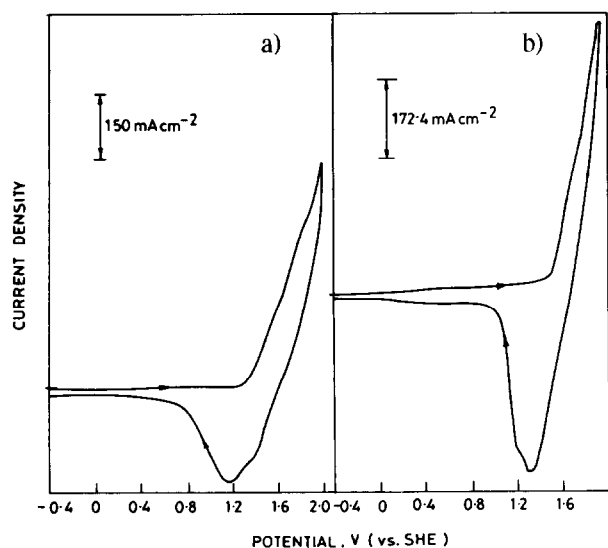


Fig. 2. Cyclic voltammograms for a HPC graphite electrode in 18.0 M HF: (a) aqueous solution, and (b) aqueous methanolic (90 vol.%) solution. Scan rate = 40 mV s<sup>-1</sup>.

The composition of aqueous methanolic HF solutions can be varied by changing the concentration of HF as well as that of methanol. The composition was adjusted in two ways in the present work. In the first method, the HF concentration was varied by directly mixing the 20.0 M aqueous HF solutions and methanol. With this approach, the methanol concentration decreases with increasing HF concentration. In the second method, the HF concentration was held constant, at 15.0 M level, and the methanolic content alone was varied. The voltammetric responses obtained under both these conditions are presented.

The electrochemical cells, counter and reference electrodes, electrochemical instrumentation and experimental procedures were the same as those described earlier [18,19].

### 3. Results and discussion

#### 3.1. Cyclic voltammetric studies

A direct comparison was made of the cyclic voltammetric (CV) responses of intercalation/de-intercalation processes in aqueous HF and aqueous methanolic HF solutions containing 1.0 to 18.0 M HF. In these solutions, the methanol content was varied from 95 to 10%, respectively. CV results in these media indicated the initiation of intercalation at ~1.4 V versus standard hydrogen electrode (SHE). De-intercalation occurred at around the same potential. At low HF concentrations, however, the intercalation/de-intercalation processes were found to be less efficient. The efficiency improved for 10.0 M HF solutions onwards. Typical cyclic voltammograms in 10.0 M HF aqueous and 10.0 M HF aqueous methanolic solutions are presented in Fig. 1(a) and (b), respectively, for direct comparison. The intercalation/de-intercalation charges were evaluated by integrating the area under the CV responses; the data are summarized in Table 1.

In aqueous HF solutions, the intercalation/de-intercalation efficiency (as measured by the ratio of de-intercalation charge,  $Q_c$ , and intercalation charge,  $Q_a$ ) is found to vary from 5 to over 50%. Beyond 15.0 M HF aqueous solution, this ratio actually decreases slightly with increasing HF concentration. In aqueous methanolic HF solutions, the intercalation/de-intercalation efficiency increases from 11 to 72% with increase in the HF concentration (Table 1).

In concentrated HF solutions (> 10.0 M HF), the cathodic de-intercalation peak is found to split into two closely spaced ones, as shown in Fig. 2. This separation is less distinguishable at slow sweep rates, but becomes more distinct at higher sweep rates (Fig. 3). The splitting of the cathodic process is probably connected with some form of stage transitions during intercalation/de-intercalation processes. Further analysis of this behaviour has not been attempted.

The intercalation/de-intercalation processes can indeed be repeated a number of times. A typical multi-sweep CV response in 10.0 M HF aqueous methanolic solution is pre-

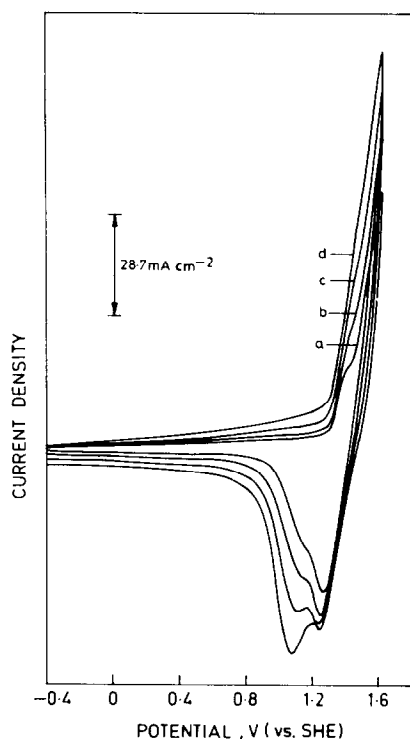


Fig. 3. Effect of sweep rate on cyclic voltammogram of HPC graphite electrode in 10.0 M HF aqueous methanolic (50 vol.%) solution. Scan rate ( $\text{mV s}^{-1}$ ) = (a) 40, (b) 80, (c) 160 and (d) 320.

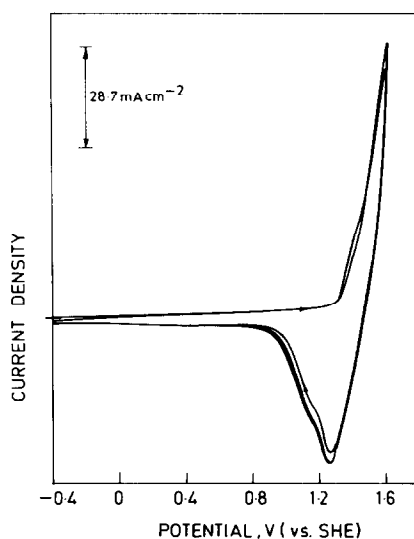


Fig. 4. Multi-sweep cyclic voltammogram of HPC graphite electrode in 10.0 M HF aqueous methanolic (50 vol.%) solution. Scan rate =  $40 \text{ mV s}^{-1}$ .

sented in Fig. 4. The charge/discharge cycles are highly reproducible.

All the cyclic voltammetric results presented above indicate that the charge recovery ratio improves with increasing HF concentration, as well as methanol concentration. To evaluate the effect of methanol content at a constant HF concentration, a separate set of CV responses were performed in 15.0 M HF solutions. In this medium, the vol.% of methanol was varied from 20 to 1%. The responses were quite similar

to those presented in Figs. 1 to 4. Nevertheless, the intercalation/de-intercalation charges and charge recovery ratios were found to vary significantly with methanol content. These results are summarized in Table 2. Maximum charge recovery efficiency was found in aqueous HF solutions that contained about 5 vol.% methanol.

### 3.2. Potentiostatic current–time transients

The CV results presented above indicate that the intercalation/de-intercalation potentials are not particularly sensitive to the methanol content. Fairly similar rates of intercalation are found around 1.6 V in the media. De-intercalation completed around 1.0 V. By setting these limits for

Table 2

Intercalation and de-intercalation charges ( $Q_a$  and  $Q_c$ ) and their ratios from CV studies of a HPC graphite electrode in 15.0 M HF aqueous methanolic solutions

Vol.% methanol	$Q_c$ ( $\text{mC cm}^{-2}$ )	$Q_a$ ( $\text{mC cm}^{-2}$ )	$Q_c/Q_a$
20	2011.52	3040.20	0.6616
15	2298.80	3390.72	0.6780
10	2586.24	3637.91	0.7109
5	2758.62	3770.00	0.7317
4	3161.42	4515.12	0.7009
3	2951.64	4598.40	0.6419
2	3006.23	4742.12	0.6339
1	2276.25	3592.52	0.6336

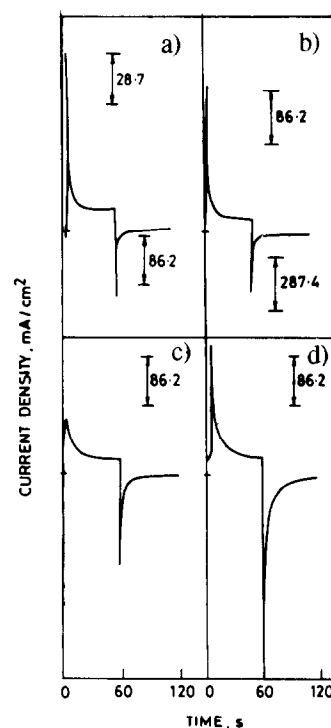


Fig. 5. Double potential sweep current–time transients ( $E_a = 1.6 \text{ V}$  and  $E_c = 1.0 \text{ V}$ ) for HPC graphite electrode. Aqueous HF solutions: (a) 10.0 M, and (b) 15.0 M; HF aqueous methanolic solutions: (c) 10.0 M, and (d) 15.0 M.

Table 3

Intercalation and de-intercalation charges and their ratios from current–time transient studies of a HPC graphite electrode in aqueous and aqueous methanolic HF solutions

Solution	Concentration (M)	$Q_c$ (mC cm <sup>-2</sup> )	$Q_a$ (mC cm <sup>-2</sup> )	$Q_c/Q_a$
Aqueous	1	16.00	192.00	0.0833
	5	154.00	690.00	0.2231
	10	460.00	977.00	0.4708
	15	1340.90	2521.00	0.5303
	18	2146.00	4176.00	0.5138
Aqueous methanol	1	4.59	47.01	0.0976
	5	181.90	1436.70	0.1266
	10	804.50	1781.50	0.4515
	15	2252.80	3304.50	0.6817
	18	2870.00	3874.50	0.7397

Table 4

Intercalation and de-intercalation charges ratio ( $Q_c/Q_a$ ) from current–time transient studies of a HPC graphite electrode in 15.0 M HF aqueous methanolic (25 vol.%) solutions as a function of step time and cycle number

Cycle number	Step time (min)		
	1	3	5
1	0.6260	0.6100	0.5227
2	0.7700	0.6041	0.5676
3	0.8620	0.7143	0.5676
4	0.8813	0.7000	0.5676
5	0.8810	0.7000	0.5676

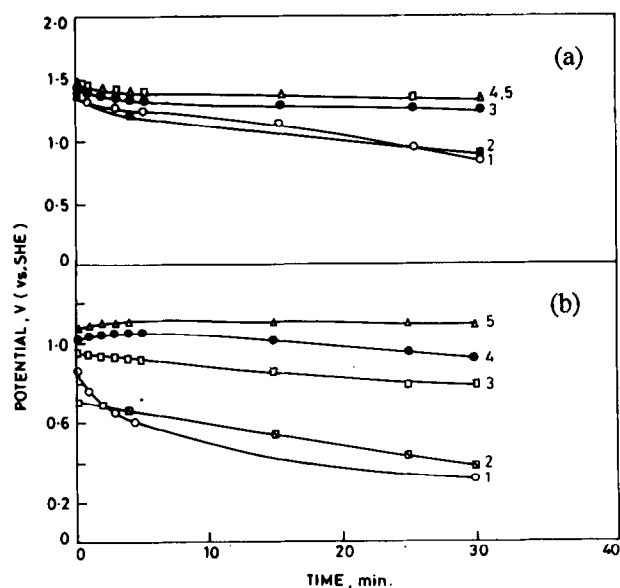


Fig. 6. Decay in open-circuit potential of HPC graphite electrode in aqueous HF solutions for 7 min after polarization at: (a) 1.6 V, and (b) 1.0 V. HF concentration (M): (1) 1.0; (2) 5.0; (3) 10.0; (4) 15.0, and (5) 20.0.

the intercalation/de-intercalation potentials, the current–time responses for charge/discharge cycles were obtained. Typical current–time responses for 10.0 and 15.0 M HF solutions

are presented in Fig. 5(a) and (b), respectively. For the purposes of comparison, the same responses for the same HF concentrations in aqueous methanolic solutions are presented in Fig. 5(c) and (d), respectively. The similarity in the current–time responses is quite obvious. The intercalation/de-intercalation charges and charge-recovery ratios in both aqueous HF and aqueous methanolic HF solutions with varying HF concentration are summarized in Table 3. The intercalation/de-intercalation efficiency is once again found to be much better in aqueous methanolic HF solutions (Table 3). There is also a linear correspondence between the  $Q_c/Q_a$  values obtained from the CV (Table 1) and the potentiostatic current–time transient (Table 3) techniques. This observation lends further evidence of the reproducibility of the experiments presented here.

The potential-step experiments could also be repeated for at least 10 cycles in both aqueous HF and aqueous methanolic HF solutions. The time of each charge/discharge step could also be increased by up to 5 min during each cycle. In these experiments, charge/discharge efficiency in aqueous HF solutions does not vary significantly with cycle number. In aqueous methanolic HF solutions, a significant improvement in charge/discharge efficiency could indeed be noticed when intercalation/de-intercalation cycles were repeated at shorter time intervals (Table 4).

### 3.3. Open-circuit potential decay (OCPD)

The open-circuit potential (OCP) of the electrode–electrolyte system before and after de-intercalation provides an indication of the reversibility, or irreversibility, of the surface processes that are involved. Hence, some OCP measurements were carried out for the graphite electrode in both aqueous HF and aqueous methanolic HF media. Before intercalation, the OCP of graphite in HF solutions was found to be about 0.4 to 0.5 V. This value increases with HF concentration. The OCP is also quite insensitive to the methanol content before intercalation.

The OCP of the graphite electrode after intercalation at 1.6 V for 7 min in aqueous HF solutions of different acid concentrations is presented in Fig. 6(a). After intercalation, the OCP remains well above 1.0 V in all the cases. The OCP decays much faster in dilute HF solutions. A qualitatively similar decay in OCP was observed in aqueous methanolic HF solutions, see Fig. 7(a). In this medium with dilute HF solutions, the OCP decays below 1.0 V within shorter intervals of time (curves (1) and (2) in Fig. 7(a)). At higher HF concentrations, however, the OCP after intercalation exhibits better stability at around 1.5 V (curves (3) and (4) in Fig. 7(a)).

By contrast, there is a significant difference in the OCP decay patterns of de-intercalated electrodes in aqueous HF and aqueous methanolic HF solutions (cf., Figs. 6(b) and 7(b)). In aqueous HF solutions with a high acid concentration, the OCP remains close to or even higher than 1.0 V. The rest potential value close to 0.5 V, noticed before intercala-

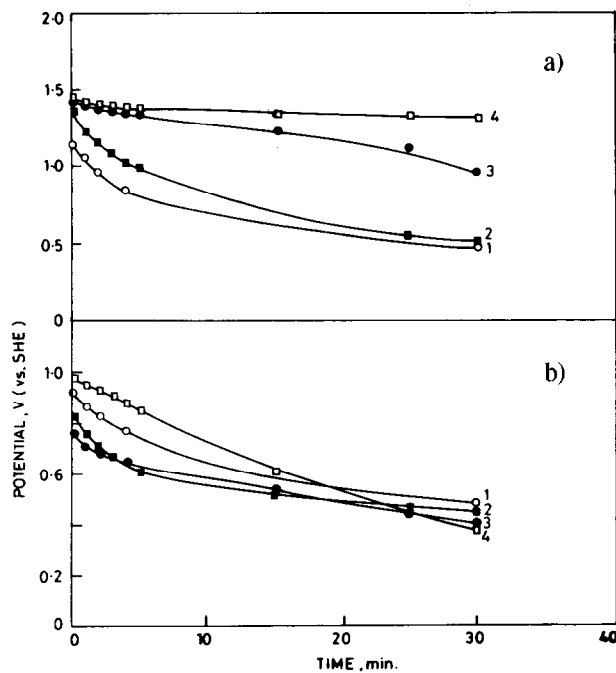


Fig. 7. Decay of open-circuit potential of HPC graphite electrode in HF aqueous methanolic solutions for 7 min after polarization at: (a) 1.6 V, and (b) 1.0 V. HF concentration (M) = (1) 1.0; (2) 5.0; (3) 10.0, and (4) 15.0.

tion, is achieved only in very dilute HF solutions (Fig. 6(b)). In aqueous methanolic HF solutions of all concentrations, however, the OCP after de-intercalation decays steadily to the original rest potential value of  $\sim 0.5$  V (Fig. 7(b)). This is a clear indication that some irreversible surface transformation occurs during intercalation/de-intercalation processes in aqueous HF solutions. The extent of this type of irreversible surface transformation is much less in aqueous methanolic HF solutions.

### 3.3. Scanning electron microscopic investigations

The actual cause of the observed improvements in the reversibility of the charge recovery and the reproducibility of the OCP decay responses in aqueous methanolic HF solutions, when compared with aqueous HF solution, becomes apparent from scanning electron microscopy (SEM) investigations. The high-purity, commercial (HPC) graphite electrode employed in the present work is not attacked severely in HF solutions provided it is not electrochemically polarized. The electron micrograph presented in Fig. 8(a), for example, shows the scratch lines present on the initial, polished surface. By contrast, large pits develop when the electrode is subjected to fluoride ion intercalation in aqueous HF solutions. This is accompanied by a significant increase in the surface roughness, as shown in Fig. 8(b). On the other hand, the same electrode subjected to similar polarization in aqueous methanolic HF solutions exhibits a lesser degree of surface roughening (Fig. 8(c)). Both number and size of the pits are much reduced.

Electron micrographs obtained after de-intercalation demonstrate the solvent effect even more clearly (Fig. 9). The irreversible surface damage appears to proceed during both the intercalation and de-intercalation processes in aqueous HF solutions (Fig. 9(a)). In aqueous methanolic HF solutions, there is no significant increase in surface roughening during de-intercalation (Fig. 9(b)). Comparison of electron micrographs for the same surface at higher magnifications (see Fig. 9(c), (d)) illustrates this difference even more sharply.

In summary, the SEM studies clearly indicate that methanol reduces significantly the irreversible degradation of graphite electrode surfaces during intercalation and de-intercalation processes.

### 3.4. X-ray diffraction measurements

X-ray diffraction (XRD) analysis was performed to characterize the intercalation/de-intercalation processes. In aqueous HF solutions, a new XRD signal was obtained at a 'd' value of  $6.529$  Å. This corresponds to the first-stage fluoride intercalated graphite. The signal intensity does not disappear completely even after prolonged de-intercalation in this medium. In aqueous methanolic HF solutions, a signal for a first-stage fluoride intercalated graphite is again observed in the same 'd'-value region. After de-intercalation in this medium, however, this signal disappears completely. These experiments indicate clearly the irreversible trapping of fluoride ions during intercalation/de-intercalation processes in aqueous solutions.

## 4. Discussion

From the point of view of intercalation/de-intercalation efficiency, the above experimental results suggest that aqueous methanolic HF solution is better than aqueous HF solution for the following reasons. The minimum anodic potential required for intercalation is slightly lower in a methanol-water mixture (for example, 1.3 V for 15.0 M HF) than in an aqueous solution (i.e., 1.5 V in 15.0 M HF). The charge-recovery ratio ( $Q_c/Q_a$ ), or reversibility, of the intercalation/de-intercalation process is also higher in a water-methanol mixture, as evaluated by cyclic voltammetry (Table 1) and potentiostatic current-time transients (Table 3). The de-intercalation process appears to proceed towards completion in aqueous methanolic solution (Fig. 7) when compared with aqueous solution (Fig. 6) since, in the former case, the OCP decays much faster towards lower values which are characteristic of graphite itself. Scanning electron micrographs obtained after polarization in a water-methanol mixture reveal a much lower level of surface degradation than is observed after polarization in aqueous media (cf., Figs. 8 and 9). Finally, XRD data also suggest a more complete de-intercalation in aqueous methanolic HF solutions.

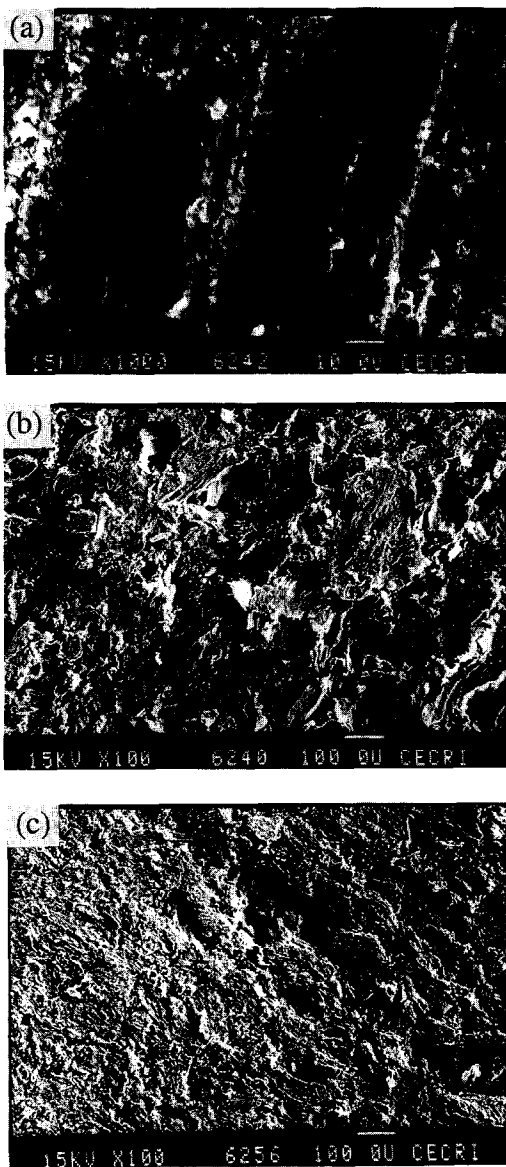


Fig. 8. Electron micrographs of HPC graphite electrode: (a) fresh surface,  $\times 1000$ ; intercalated in 15.0 M HF at 1.6 V for 7 min; (b) aqueous solution,  $\times 100$ , and (c) aqueous methanolic solution,  $\times 100$ .

There are three modes, at least, by which the solvent molecules can influence the intercalation/de-intercalation reactions on graphite. First, solvent molecules can affect both the dissociation of HF and the solvation of  $H^+$  and  $F^-$  ionic species and, hence, will modify the rate of the intercalation/de-intercalation reaction. Second, solvent molecules can chemisorb competitively on the electrode surface to displace water and, hence, restrict the electrochemical process. Finally, chemisorbed solvent molecules can prevent to a significant extent the formation of graphite oxide and oxygen evolution.

The predominant effect of methanol arises mainly from the preferential adsorption of the compound on the graphite surface. Such adsorption can reduce significantly the chemical attack of HF on the active sites and defects of the polished

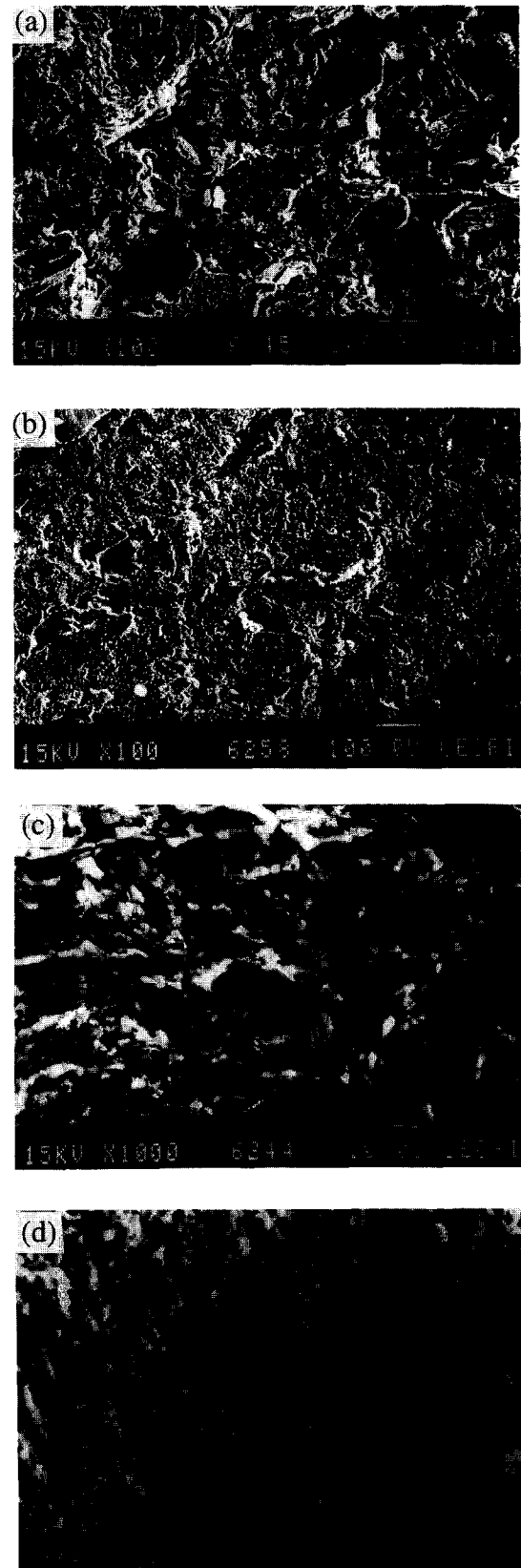


Fig. 9. Electron micrograph of HPC graphite electrode de-intercalated in 15.0 M HF at 1.0 V for 7 min: (a) aqueous solution,  $\times 100$ ; (b) aqueous methanolic solution,  $\times 100$ ; (c) aqueous solution,  $\times 1000$ , and (d) aqueous methanolic solution,  $\times 1000$ .

graphite surface. The methanol adsorption can also inhibit the formation of oxygen-based redox functional groups on the active sites of graphite electrodes. Accordingly, lower redox currents are noticed in the middle potential region at the same HF concentration levels in water–alcohol mixtures. In addition to this favourable impact, methanol also inhibits graphite oxide formation and oxygen-evolution reactions at more anodic potentials. This is possibly responsible for the higher  $Q_c/Q_a$  ratio under both potentiodynamic (CV) and potentiostatic current–time transient conditions.

Reversible intercalation/de-intercalation processes can lead to the exfoliation of graphite lattices. For an intercalation process involving a small anion such as  $F^-$  ion, however, this lattice expansion may not be the main cause of irreversible surface degradation. The latter process, in aqueous HF solutions, would arise mainly from irreversible oxide formation on the surface as well as in the interior of the graphite lattice. The oxygen is supplied by water molecules on the electrode surface and inside the graphite lattice. By preferential adsorption, methanol suppresses to a significant extent the availability of water on the graphite surface. This appears to be the main reason for less surface deterioration, more reversible OCP decay behaviour, and complete de-intercalation.

Adsorption of methanol requires only a very small concentration of the compound in the aqueous electrolyte solution. The evaluation of CV responses in 15.0 M HF solution containing different methanol concentrations (Table 2) indicates that, for maximum efficiency, a minimum of 5 vol.% methanol is required in the electrolyte solution. This fairly high percentage of methanol suggests that adsorption is not the only influence of this solvent molecule. Methanol is a solvent with a lower dielectric constant. The  $F^-$  ion concentration cannot be enhanced because of dissociation of the weaker HF. The acceptor number of methanol is 41.3 and the acceptor number of water is 54.8 [20]. Hence, even in water–methanol mixtures, fluoride will remain as a predominantly hydrated species. It follows that the intercalated species in water–methanol mixtures would also be the same hydrated  $F^-$  ion. This is also apparent from the same 'd' value obtained for the intercalated species in XRD measurements. Methanol in low concentrations, however, can play another significant role by breaking the structure of hydrated water [21]. Such breaking would make available a greater concentration of hydrated  $F^-$  ions for intercalation. This is the second favourable influence of methanol on the intercalation/de-intercalation processes.

## 5. Conclusions

The present investigations suggest that reversible intercalation/de-intercalation can be conducted more efficiently in aqueous HF solutions that contain methanol. The efficiency increases significantly with HF concentration. An optimum

level of around 5 vol.% methanol improves significantly the intercalation/de-intercalation behaviour with minimum surface degradation. The predominant influence of methanol seems to be preferential adsorption on graphite surfaces that, in turn, prevent access to water molecules for oxygen evolution and graphite oxide formation. The structure-breaking effect of methanol in aqueous methanolic HF solutions also appears to be important. Similar favourable solvent effects may also be prevalent in other graphite intercalation systems. This aspect deserves further attention.

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## References

- [1] R. Payne, *Adv. Electrochem. Electrochem. Eng.*, **7** (1970) 1.
- [2] C.K. Mann, *Electroanal. Chem.*, **1** (1969) 51.
- [3] D. Billaud, A. Proñ, F.L. Vogel and A. Hérol, *Mater. Res. Bull.*, **15** (1980) 1627.
- [4] D. Billaud, A. Proñ and F.L. Vogel, *Synth. Met.*, **2** (1980) 177.
- [5] M.S.R. Cader, S. Karunanithy and F. Aubke, *Synth. Met.*, **30** (1989) 9.
- [6] M. Inagaki, T. Mitsuhashi and V. Soneda, *J. Chim. Phys.*, **84** (1987) 1439.
- [7] N. Watanabe and M. Fukuda, *US Patent No. 3 536 532* (1970); *US Patent No. 3 700 502* (1972).
- [8] Y. Kita, N. Watanabe and Y. Fujii, *J. Am. Chem. Soc.*, **19** (1979) 3832.
- [9] N. Watanabe, *Solid State Ionics*, **1** (1980) 87.
- [10] N. Watanabe, R. Hagiwara and T. Nakajima, *J. Electrochem. Soc.*, **131** (1984) 1980.
- [11] N. Watanabe, T. Nakajima and H. Touhava, *Graphite Fluorides*, Elsevier, Amsterdam, 1988.
- [12] N. Watanabe, T. Nakajima and R. Hagiwara, *J. Power Sources*, **20** (1987) 87.
- [13] R. Hagiwara, T. Nakajima and N. Watanabe, *J. Electrochem. Soc.*, **135** (1988) 2128.
- [14] T. Nakajima, K. Moriya, R. Hagiwara and N. Watanabe, *Electrochim. Acta*, **30** (1985) 1541.
- [15] T. Nakajima, R. Hagiwara, K. Moriya and N. Watanabe, *J. Power Sources*, **20** (1987) 93.
- [16] H. Takanaka, M. Kawaguchi, M. Lerner and N. Bartlet, *J. Chem. Soc., Chem. Commun.*, (1987) 1987.
- [17] F. Beck and H. Krohn, *J. Power Sources*, **12** (1984) 9.
- [18] M. Noel, R. Santhanam and M.F. Flora, *Electroanalysis*, (1994) in press.
- [19] M.F. Flora, *Ph.D. Thesis*, Alagappa University, Karaikudi, India, 1993, Ch. 4.
- [20] V. Gutmann, *Electrochim. Acta*, **21** (1976) 661.
- [21] G.T. Hefter, *Rev. Inorg. Chem.*, **10** (1989) 185.