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Effect of polypyrrole film on the stability and electrochemical activity of fluoride based graphite intercalation compounds in HF media

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Fluoride intercalation/deintercalation cycles on commercially available high purity graphite electrodes leads to powder formation and electrode damage. Formation of polypyrrole films of optimum thickness by potential cycling on the graphite surface before fluoride intercalation leads to good mechanical stability to the electrode during intercalation/deintercalation cycles. The intercalation potential shifts by 200 mV in the positive direction. The intercalation and deintercalation charges (Q_a, Q_c) also decrease slightly. However the charge recovery ratio (Q_c/Q_a) improves significantly. Since the polypyrrole layer is compact on the graphite surface, the present study indicates that the film offers mechanical stability to the graphite film without affecting the electronic conductivity of the surface. F^- ion transport through the film also occurs with a small overvoltage.

1. Introduction

Redox polymer films, as well as conducting polymer films, have been previously employed to protect semiconducting surfaces during photoexcitation [1–5]. Recently, a conducting polypyrrole codeposit was shown to protect PbO_2 deposits prepared on glassy carbon electrodes [6]. Codeposition of polypyrrole with a redox species, namely nickel cyclan [7], and inert filling material, namely TiO_2 particles [8], were also reported recently. However, there is apparently no reported work on the effect of polypyrrole film on an intercalation/deintercalation process in which intercalent transfer through the conducting polymer layer is a necessary step.

In a recent study [9], it was found that in 15.0 M HF aqueous solutions containing 25% (v/v) methanol, satisfactory intercalation and deintercalation of fluoride ions on graphite could be achieved for the first few cycles. However, the graphite electrode became mechanically unstable after two or three charge/discharge cycles. The effect of polypyrrole film on the stability and the charge/discharge behaviour of the graphite electrode in 15.0 M HF aqueous methanolic solutions is the subject matter of the present work.

2. Experimental details

A high purity commercial graphite electrode (HPC grade, Graphite India Limited, India) sized into 3 mm diameter rods and tight-fitted into a Teflon holder served as the working electrode. Platinum foil served as the counter electrode.

For the voltammetric studies and preparation of polypyrrole coating, an H-type glass cell with a SCE reference electrode was used. For intercalation/deintercalation studies in HF solutions, a single compartment polypropylene cell with $Pd–H_2$ reference electrode was used [9]. LR grade pyrrole (SRL, India) was freshly distilled before use. All other chemicals used were of AR grade.

The polypyrrole coating procedure [6], involved potential cycling in 1.0 M KNO_3 solution containing 5 mM pyrrole from 0.0 to 0.8 V for 5 or 10 cycles at a sweep rate of 20 mV s^{-1}. During the voltammetric response of polypyrrole formation (Section 3.1) 50 mM pyrrole was used. All the experiments were carried out at 303 ± 1 K. The reproducibility of the results were verified by repeating each experiment at least three times. The variation of peak potentials within ±10 mV and peak current within 3% could be achieved under these experimental conditions.

3. Results

3.1. *Polypyrrole formation*

Since polypyrrole film formation can exhibit some surface specific effects, a few voltammetric studies were carried out on the graphite electrodes employed in the present work. Typical multisweep CV responses for 50 mM pyrrole in 1.0 M KNO_3 between the potential limits of 0.0–1.0 V at a sweep rate of 20 mV s^{-1} are presented in Fig. 1(a). The typical anodic peak observed on GCE [6] under similar conditions appears much broader on this high purity graphite surface. Interestingly, there is significant anodic

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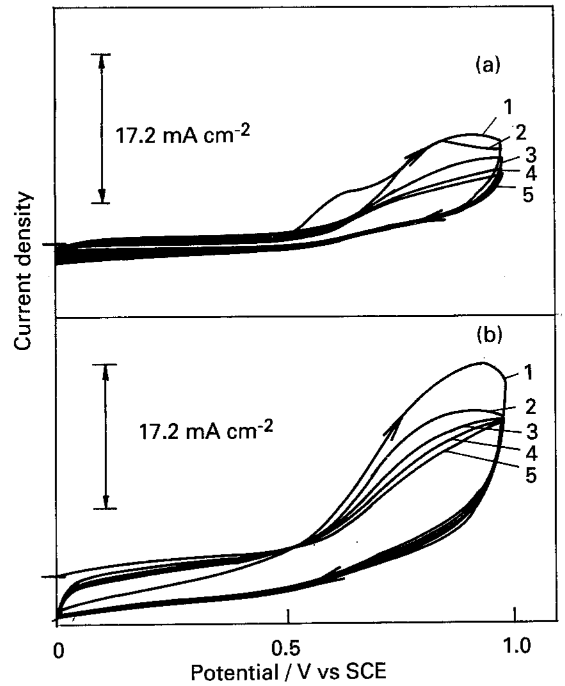

Fig. 1. Multisweep CV (for 5 cycles) in 1.0 M KNO_3 solution containing 50 mM pyrrole on fresh high purity graphite before (a) and after (b) intercalation in 15.0 M HF aqueous–methanolic (25% v/v) solution at 1.6 V for 3 min; $v = 20\,mV\,s^{-1}$.

current around 0.5 V itself and a distinct prepeak is noticed around 0.650 V in the first sweep, which disappears in the subsequent sweeps (Fig. 1(a)). The passivation effect is also noticed on the graphite electrode if the anodic limit is held beyond 0.850 V. The steady decline in the anodic current with increasing sweep number when the anodic potential limit exceeds 0.850 V (Fig. 1(a)) is due to the insulating polymer formation beyond this limit [6].

Figure 1(b) is the multisweep voltammetric response obtained on a fluoride intercalated graphite electrode prepared by anodic polarization at 1.6 V for 3 min in 15.0 M HF aqueous–methanolic solution. The experimental conditions for polypyrrole formation were the same for Fig. 1(b) as for Fig. 1(a). Apart from significantly higher anodic current and the absence of a prepeak around 0.650 V, the multisweep voltammetric responses on fluoride intercalated graphite electrodes are similar to those on the graphite electrodes themselves.

These voltammetric responses thus indicate that polypyrrole films can be obtained on graphite, as well as fluoride intercalated graphite electrodes.

3.2. *Studies on polypyrrole coated graphite electrode*

A polypyrrole film was coated on a graphite electrode by cycling it between 0.0 and 1.0 V at $20\,mV\,s^{-1}$, 5 and 10 times, respectively, to prepare electrodes with two different film thicknesses. Figure 2(a) shows the typical current potential response in this conducting film forming potential region for five cycles. The voltammetric responses in 15.0 M HF aqueous–methanolic solution is presented in Fig. 2(b). The minimum anodic limit required for observing deintercalation on a film coated electrode is 1.6 V (Fig. 2(b)) whereas it is only 1.4 V on a bare graphite electrode [9]. The Q_a and Q_c values obtained by integrating the anodic and cathodic regions of the CV response on a film coated electrode is also slightly lower (Table 1). The Q_c/Q_a value remains at a significantly higher level for the film coated electrode (Table 1). The thicker polypyrrole film obtained by ten potential cycles in the pyrrole medium leads to slightly lower currents and correspondingly lower intercalation/deintercalation charges (Table 1).

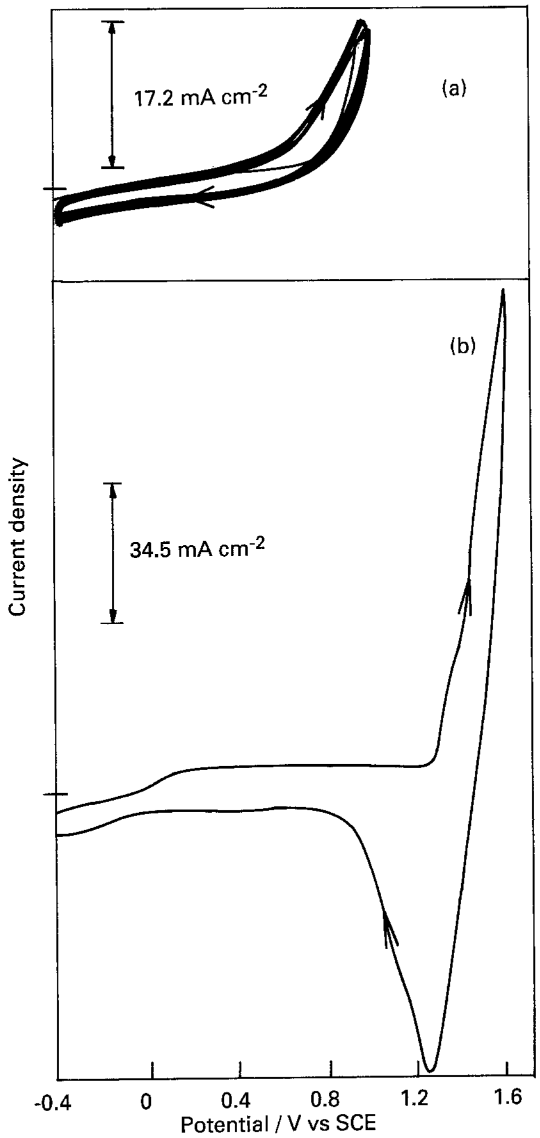

Fig. 2. (a) Multisweep CV (for 5 cycles) in 1.0 M KNO_3 solution containing 50 mM pyrrole of fresh high purity graphite; $v = 20\,mV\,s^{-1}$. (b) CV of high purity graphite after the above treatment in 15.0 M HF aqueous–methanolic (25% v/v) solution; $v = 40\,mV\,s^{-1}$.

The potentiostatic intercalation/deintercalation studies at 1.6 and 1.0 V, respectively, were carried out with intercalation times of 1, 3 and 5 min. Typical double-potential step *i*/*t* transients obtained at the first, fifth and tenth cycles with these three intercalation times are presented in Fig. 3 for the graphite electrode coated with polypyrrole using five cycles. The intercalation/deintercalation process on this electrode continues, even after ten potential cycles, when

Table 1. Ratio of intercalation and deintercalation charges from CV, in 15.0 M HF aqueous methanolic (20% v/v) solutions, of fresh high purity graphite and HPCG pyrrole coated before and after intercalation

$v = 40\,\mathrm{mV\,s^{-1}}$

	Nature of graphite	*Potential limit for appearance of deintercalation*	*Number of cycles (pyrrole coating)*	Q_c /mC cm^{-2}	Q_a /mC cm^{-2}	Q_c/Q_a
1	Fresh	1.4	–	1207	1824	0.66
2	Fresh	1.6	5	491	658	0.75
3	Fresh	1.6	10	385	523	0.74
4	Intercalated	1.8	5	124	219	0.57

compared to bare graphite electrodes [9], which show mechanical deterioration after three to five potential cycles. The polypyrrole coated electrodes used here develop a grey colour after ten cycles, but the electrode surface still remains smooth, intact and electroactive.

Graphite electrodes coated with five and ten polypyrrole formation cycles exhibit good charge recovery ratios if the intercalation/deintercalation processes are repeated at a shorter time interval of 1 min (Table 2). With the electrode of 10 polypyrrole coating cycles (Table 2), this ratio can reach 80%. Even on a thinner polypyrrole coated electrode (five polypyrrole formation cycles) the recovery ratio improves with sweep number and reaches 80% in the tenth cycle. Individual Q_c, Q_a values (not tabulated here) slightly decrease with film thickness.

With increasing intercalation/deintercalation times, however, the Q_c/Q_a values on film coated electrodes drop quite sharply for both the electrodes. With 3 and 5 min of intercalation/deintercalation times for example, the recovery ratio falls to 50% or even lower (Table 2).

3.3. *Studies on polypyrrole coated fluoride intercalated graphite electrodes*

In the initial phase of the present work, it was felt that polypyrrole coating on a fluoride intercalated, and thus expanded, graphite lattice would exhibit more stability and better electrochemical activity. Fig. 1(b) also showed slightly higher polypyrrole formation currents on the fluoride intercalated graphite

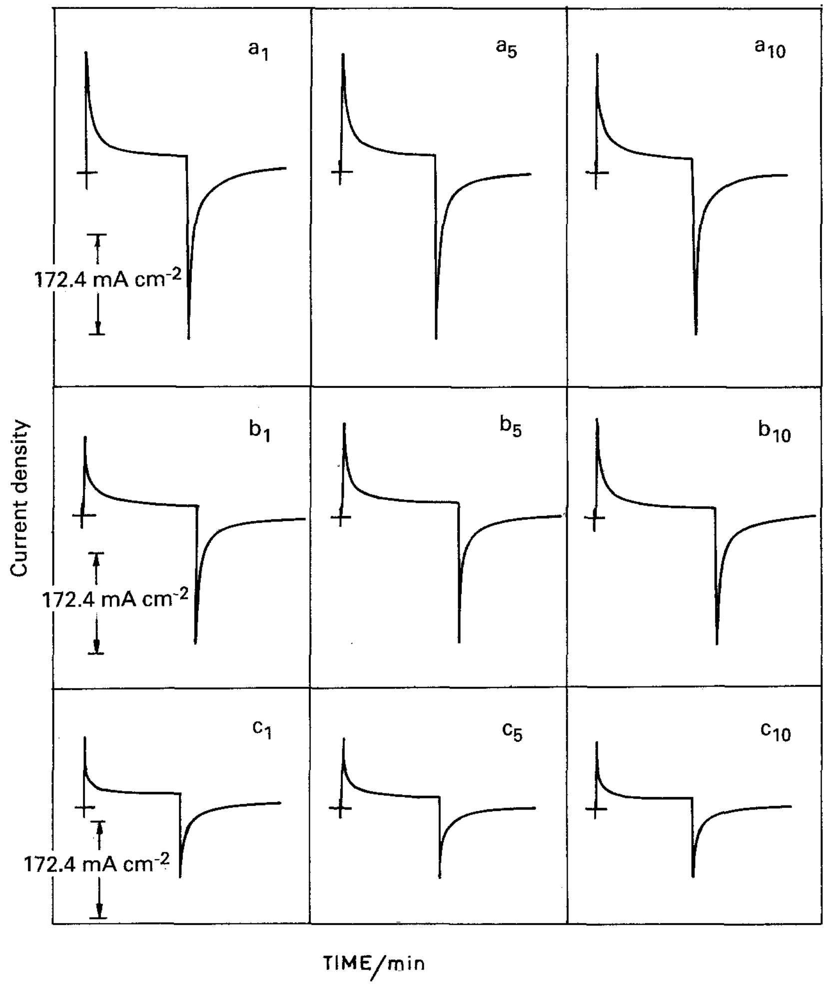

Fig. 3. Double potential step ($E_a = 1.6\,\mathrm{V}$ and $E_c = 1.0\,\mathrm{V}$) i/t transients of fresh high purity graphite (5 cycles pyrrole coated as in Fig. 2(a)) in 15.0 M HF aqueous–methanolic (25% v/v) solutions; step time/min: (a) 1, (b) 3 and (c) 5; first, fifth and tenth cycles are shown with appropriate numbers.

Table 2. Ratio of intercalation and deintercalation charges from i/t transients in 15.0 M HF aqueous–methanolic (25% v/v) solutions, of pyrrole coated fresh high purity graphite for different step time and cycle number

$E_a = 1.6\,V$ *and* $E_c = 1.0\,V$

Potential cycles in 50 mM pyrrole	*Cycle number*	Q_c/Q_a/mC cm^{-2} *for different step time*		
		1 min	*3 min*	*5 min*
5	1	0.66	0.52	0.48
5	5	0.68	0.43	0.43
5	10	0.81	0.43	0.42
10	1	0.80	0.42	0.42
10	5	0.81	0.48	0.45
10	10	0.83	0.52	0.50

surface. Typical CV responses of a polypyrrole coated graphite electrode obtained by the above procedure in 15.0 M HF aqueous–methanolic solutions, with different anodic limits, are presented in Fig. 4. Even at the 1.6 V anodic limit, no intercalation/deintercalation process is noticed on this electrode. The minimum anodic limit required for intercalation is 1.8 V (Table 1). Even at this anodic limit, Q_c, Q_a values and Q_c/Q_a ratios are much lower on this surface (Table 1). In the double potential step experiments with E_a and E_c values of 1.8 V and 1.0 V, respectively, Q_c and Q_a values are low when compared to the other electrodes. The Q_c/Q_a values change with cycle number in a random fashion (Table 3). In general there is considerable decrease in recovery ratio with increasing cycle number (Table 3). With higher intercalation/deintercalation times, the charge recovery ratio also decreases significantly (Table 3). Obtaining reproducible levels of Q_c and Q_a values also becomes quite difficult under these experimental conditions.

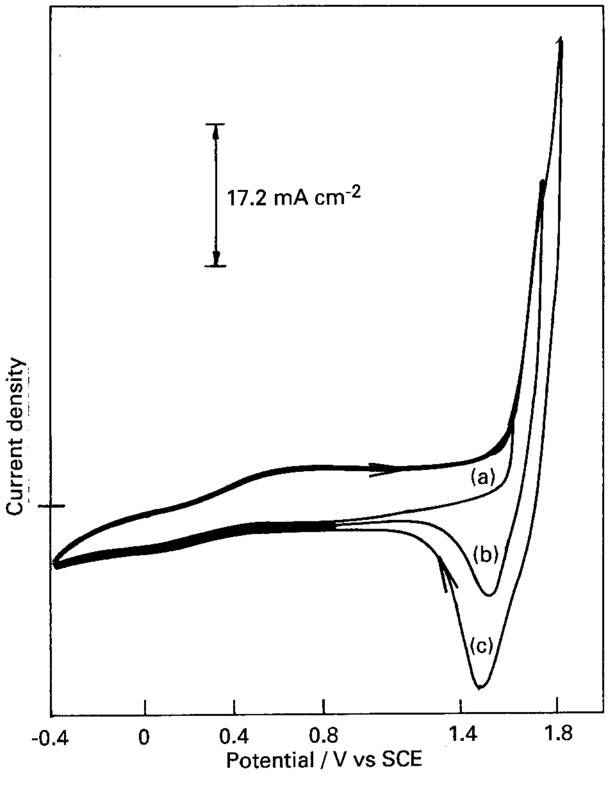

Fig. 4. CV of high purity graphite (intercalated in 15.0 M HF aqueous–methanolic (25% v/v) for 3 min and then pyrrole coated as in Fig. 2(a)) in 15.0 M HF aqueous–methanolic (25% v/v) solution; $v = 40\,mV\,s^{-1}$. Anodic limits: (a) 1.6 V, (b) 1.7 V and (c) 1.8 V.

4. Discussion

A graphite surface contains some excess active centres where polymerization can easily take place during the first cycle at 50.0 mM pyrrole concentration. This is possibly responsible for the first anodic peak (Fig. 1(a)) around 0.65 V (the reproducibility of this response was verified many times under identical experimental conditions). In the second and subsequent sweeps this oxidation peak disappears due to the absence of these active centres (Fig. 1(a)). As far as polypyrrole formation is concerned, the fluoride intercalated graphite surface, with expanded surface areas, definitely leads to high anodic polymerization currents (Fig. 1(b)).

The fact that a thin polymer coated electrode still allows an intercalation/deintercalation process, is an interesting observation of the present work. It is known that polypyrrole is electronically conducting, when prepared under the present experimental conditions. From the present studies however, it becomes apparent that this film also allows facile F^- ion transport through the film. Microscopic studies showed a compact and uniform polypyrrole film on graphite, thus excluding fluoride intercalation/deintercalation reactions proceeding through pores.

The present results indicate that F^- intercalation/deintercalation proceeds on graphite electrodes even in the presence of a uniform compact polypyrrole layer. However, the minimum potential required for intercalation is shifted by 200 mV in the positive direction, which suggests a higher energy requirement. The intercalation and deintercalation charges also decrease slightly, both under potentiodynamic (Table 1) and potentiostatic conditions (Table 2). These parameters also decrease with increasing film thickness. However, the significant improvement in the intercalation/deintercalation behaviour and stability of the surface still justifies further investigation.

Table 3. Ratio of intercalation and deintercalation charges from i/t *transients in 15.0 M* HF *aqueous–methanolic (25% v/v) solutions, of deintercalated HPCG pyrrole coated (5 cycles) for different step time and cycle number*

$E_a = 1.8\,V$ *and* $E_c = 1.0\,V$

Cycle	*Charge*/mC cm^{-2}					
	Step time 1 min			*Step time 3 min*		
	Q_c	Q_a	Q_c/Q_a	Q_c	Q_a	Q_c/Q_a
1	500	885	0.57	661	1149	0.58
5	649	839	0.77	825	1078	0.77
10	149	529	0.28	534	1480	0.36

In contrast to initial expectations, the polypyrrole film on a fluoride intercalated graphite had some extremely negative effects on the overall intercalation/deintercalation process (Section 3.3). The minimum intercalation potential shifted further by 200 mV. The charge values and charge recovery ratios dropped considerably. Even Q_c and Q_a values varied significantly when the experiments were repeated under identical experimental conditions on these electrodes. The exact cause for such negative effects, however, is not yet clear. On a fluoride intercalated graphite surface, either the pathways of intercalation/deintercalation are blocked or a more passive polypyrrole layer is formed. Further investigations would be worthwhile.

5. Conclusions

Polypyrrole films can be formed easily and reproducibly on graphite electrodes. These films allow F^- ion transport with small, but noticeable, voltage drop, thus allowing effective intercalation/deintercalation processes in 15.0 M HF aqueous–methanolic solutions. The intercalation charge decreases slightly with film thickness. This process improves the mechanical stability, as well as the charge recovery ratio. Intercalating the graphite surface before forming the polypyrrole layer, however, leads to comparatively inferior responses.

These observations raise questions for further study such as the optimum thickness of the polypyrrole layer, the mode of fluoride ion transport through the film, transformations during the charge/discharge cycles, and intercalation of other ionic species into graphite.

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