



Short communication

Surface transformations of polypropylene-graphite composite electrode material during intercalation/de-intercalation of monovalent cationic and anionic species from non-aqueous solvents

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Abstract

Surface transformations of a polypropylene-graphite composite electrode after intercalation/de-intercalation of monovalent cationic (Li^+ , Na^+ , K^+ and TBA^+) and anionic (ClO_4^- and BF_4^-) species in different non-aqueous solvents are compared under otherwise identical experimental conditions using scanning electron microscopy (SEM). Li^+ and TBA^+ cations, as well as the BF_4^- anion, display fairly high intercalation/de-intercalation efficiency and a high level of surface roughening due to the removal of horizontally-oriented graphite plates in the initial phases of cycling. Edge planes are found to be responsible for the highly reversible intercalation/de-intercalation behavior and the cycleability. © 1998 Elsevier Science S.A.

Keywords: Graphite electrodes; Intercalation; Scanning electron microscopy

1. Introduction

Scanning electron microscopy (SEM) has been employed to study the surface transformations that take place during the intercalation/de-intercalation of ionic species into highly oriented pyrolytic graphite (HOPG) [1], natural graphite [2] and carbon fibers [3]. Exfoliation and powdering are found to be considerably higher when more active graphite materials are used [4]. Transformation of exfoliated carbon fiber into graphite sheets has also been observed [5]. Finally, there have been reports of the effect of solvent media [6], cationic species [7] and graphite electrode composition [8] on the overall surface modification and stability.

It is well-known that the nature of the solvent and the intercalating ionic species play a significant role in the overall rate of intercalation, the intercalation/de-intercalation efficiency (IDE), and the overall stability of the host lattice. Nevertheless, there have been no reports of a systematic study aimed at comparing the effect of intercalating ionic species and solvent on the graphite surface transformations. In the present work, an attempt is made to evaluate the surface transformations during the intercala-

tion/de-intercalation of monovalent cationic (Li^+ , Na^+ , K^+ and tetrabutyl ammonium ion, TBA^+) and anionic (ClO_4^- and BF_4^-) species from different solvents (i.e., dimethylsulfoxide, DMSO; dimethylformamide, DMF; propylene carbonate, PC, and acetonitrile, AN) on a composite graphite electrode material that contains 20 wt.% polypropylene.

2. Experimental

A polypropylene-graphite composite electrode (CPP) with a diameter of 3 mm was embedded in a Teflon rod and was used as the working electrode. The electrode was threaded onto a copper rod which could be disconnected after electrochemical polarization, washed, dried, and directly subjected to SEM studies. Platinum and a saturated calomel electrode were used as the counter and reference electrodes, respectively. The electrode was polarized at -2.5 V for cationic intercalation, and at $+2.5$ V for anionic intercalation, for a period of 10 min in all cases. The de-intercalation potential was set at -1.4 V for cationic de-intercalation and $+1.4$ V for anionic de-intercalation for the same period of time. The electrolyte concentration in all cases was kept at 0.25 M.

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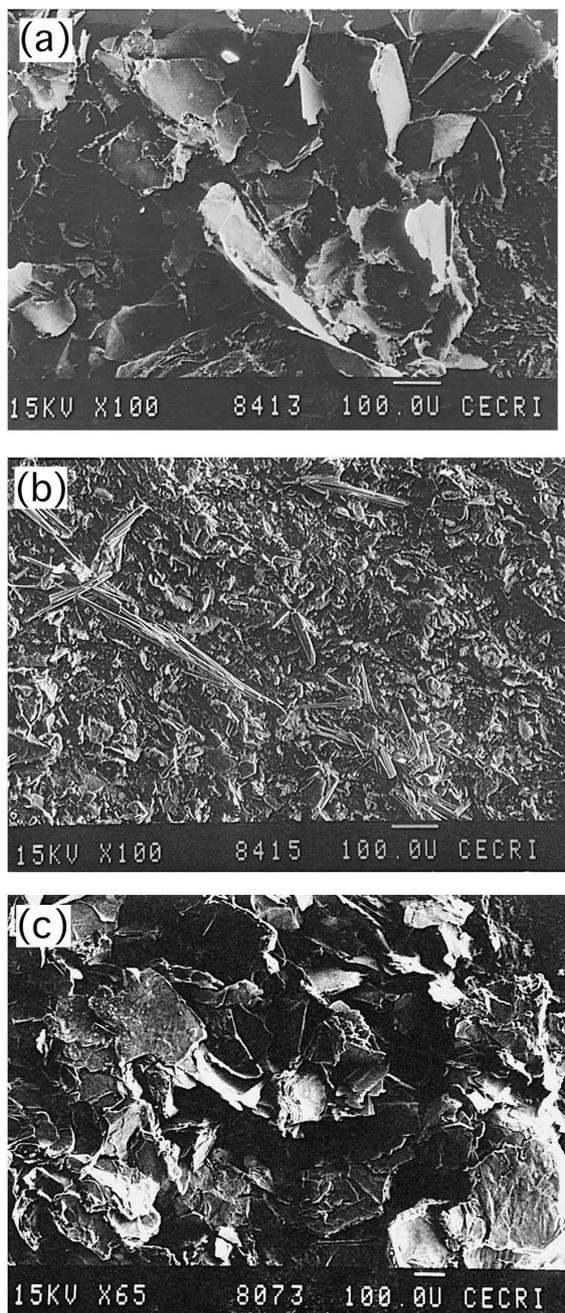


Fig. 1. The scanning electron micrographs of a CPP electrode in 0.25 M solutions containing Na^+ and K^+ perchlorate salts. Intercalation and de-intercalation for 10 min. (a) K^+ de-intercalated graphite from DMSO solvent polarized at -2.5 V and subsequently at -1.4 V $\times 100$; (b) TBA^+ intercalated graphite from DMSO solvent polarized at -2.5 V $\times 100$; (c) TBA^+ intercalated graphite from PC solvent polarized at -2.5 V $\times 100$.

Distilled AR grade solvents (DMSO, DMF, PC, AN) and freshly dried AR grade supporting electrolytes (LiClO_4 ; NaClO_4 ; KClO_4 ; tetrabutyl ammonium perchlorate, TBAP; tetrabutyl ammonium fluoborate, TBAFB) were employed throughout.

SEM was performed with a JEOL (Model 30CF) scanning electron microscope.

3. Results and discussion

3.1. Intercalation of monovalent cationic species

Cyclic voltammetric and potentiostatic polarization studies indicated that among the four cationic species, namely, Li^+ , Na^+ , K^+ and TBA^+ , the IDE was greatest for Li^+ and TBA^+ ions [9,10]. SEM studies also confirm this view. For example, during Na^+ intercalation from DMSO containing NaClO_4 , only diffused boundary lines between graphite plates were noticed after intercalation/de-intercalation cycle. The SEM micrographs show that the electrode does not undergo any noticeable roughening.

The electrode roughness increases to some extent during intercalation/de-intercalation of K^+ ions (Fig. 1a). This causes the horizontally held graphite plates to peel off from the electrode surface. Graphite plates that are strongly held in the polypropylene matrix are clearly visible. Nevertheless, the electrode surface still remains substantially smooth.

The roughness of the intercalated surface increases during Li^+ ion intercalation. Since the latter proceeds

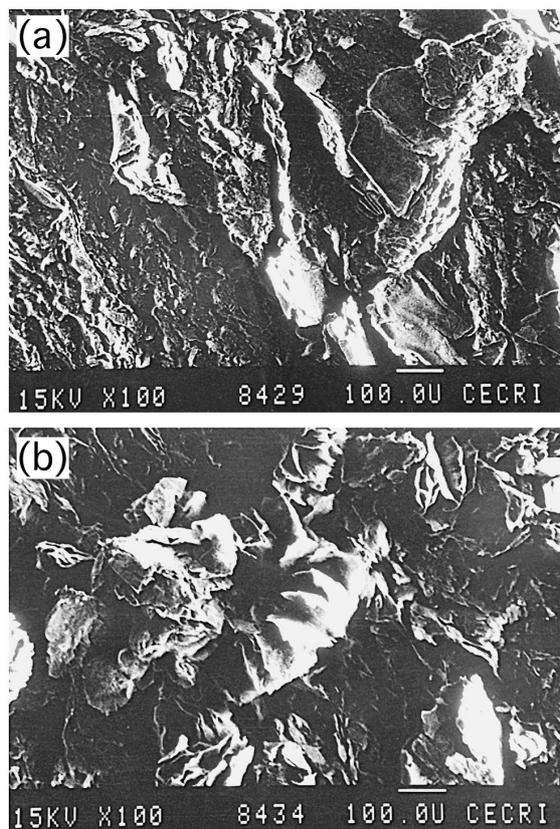


Fig. 2. The scanning electron micrographs of a CPP electrode in a given 0.25 M AN solution containing TBAP and TBAFB salts. Intercalation and de-intercalation for 10 min at $+2.5$ V and $+1.4$ V, respectively; (a) ClO_4^- intercalated graphite $\times 100$; (b) ClO_4^- de-intercalated graphite $\times 100$.

more efficiently under the same experimental conditions, loosely held horizontal graphite plates are completely removed. All the edge planes of exposed graphite plates are intercalated and hence become exfoliated. This leads to significant surface roughening.

Similar surface roughening is also noticed during the intercalation of TBA^+ cations from the same DMSO solvent (Fig. 1b). Some edge planes of fairly long graphite platelets are observed as ridges in this figure.

In general, the IDE of TBA^+ cations is $> 50\%$ for all of the three solvents employed, namely, DMSO, DMF and

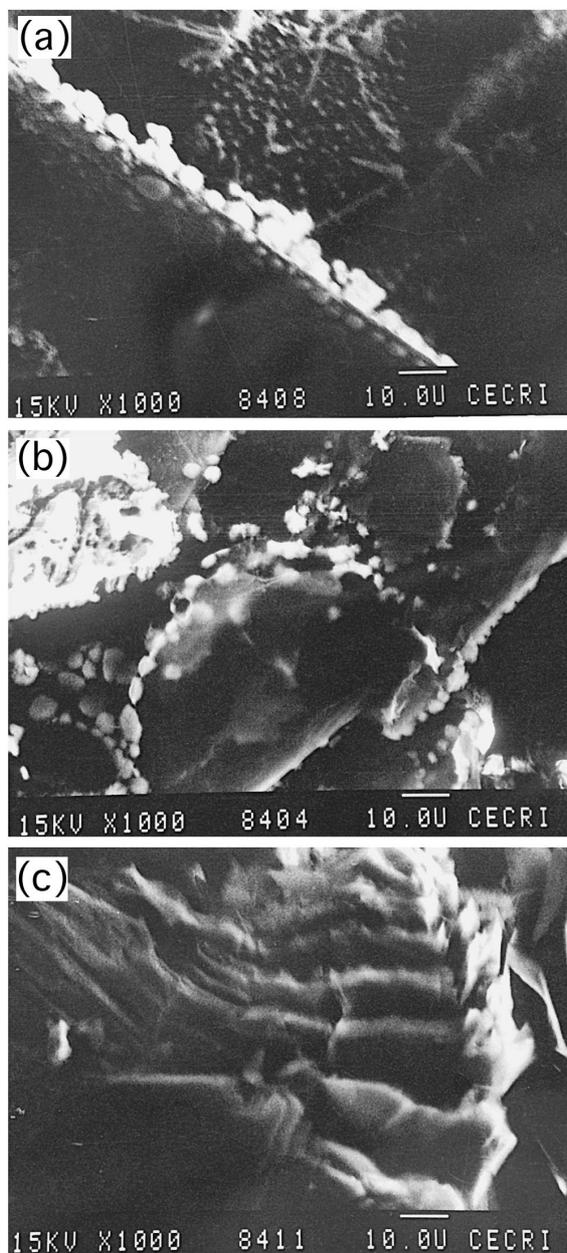


Fig. 3. The scanning electron micrographs of a CPP electrode in 0.25 M DMSO solutions containing given perchlorate salts. Intercalation and de-intercalation for 10 min at -2.5 V and -1.4 V, respectively. (a) K^+ intercalated graphite $\times 1000$; (b) Na^+ intercalated graphite $\times 1000$; (c) Na^+ deintercalated graphite $\times 1000$.

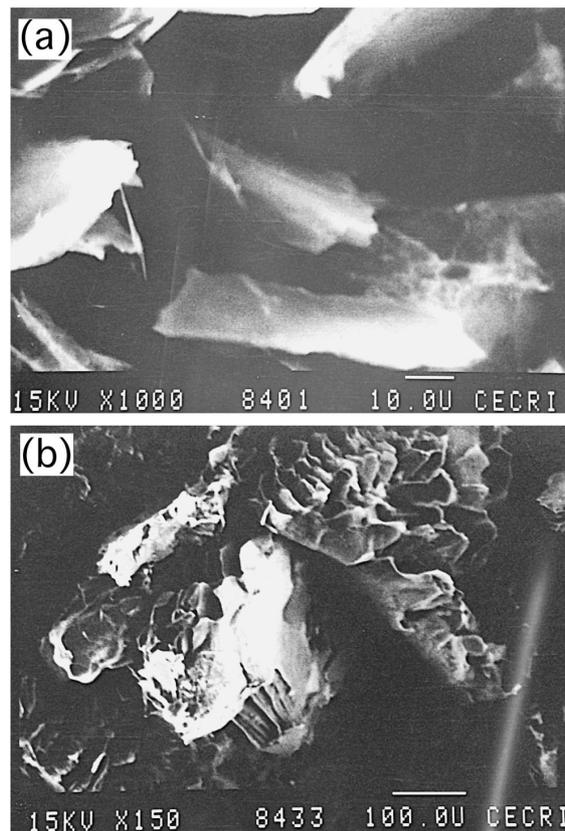


Fig. 4. The scanning electron micrographs of a CPP electrode in 0.25 M solution containing Na^+ and K^+ perchlorate salts. Intercalation and de-intercalation for 10 min. (a) Li^+ intercalated graphite from DMSO solvent polarized at -2.5 V $\times 1000$; (b) ClO_4^- deintercalated graphite from AN solvent polarized at $+2.5$ V and subsequently at $+1.4$ V $\times 150$.

PC. The surface transformations were also similar in all these cases (Fig. 1b and c). In PC (Fig. 1c) and DMF, however, the sizes of retained graphite plates are generally greater than $200 \mu\text{m}$. It appears that smaller graphite platelets are easily removed from the substrate after intercalation and exfoliation.

3.2. Intercalation of monovalent anionic species

Cyclic voltammetric studies have already indicated that solvent decomposition and related competitive processes occur simultaneously with anion intercalation and give rise to a $< 50\%$ IDE [9,10]. The SEM micrographs obtained on anion-intercalated CPP samples also substantiate this view. A typical SEM micrograph after the intercalation of ClO_4^- anion in AN solvent is shown in Fig. 2a. Fairly deep pits are clearly seen. Similar morphology is obtained after the intercalation of BF_4^- anions. During repeated cycling, vertically held graphite plates exhibit a wide variety of exfoliation patterns. An example of this behavior is given in Fig. 2b.

3.3. Some distinct micrographic patterns

3.3.1. Edges

In addition to the general patterns described above, the micrographs also exhibit some distinct surface features. For example, in weakly intercalated systems (Na^+ and K^+ ions), the graphite plates remain intact. The intercalation and resultant exfoliation proceeds on the edges of the graphite plates resulting in fairly long edges of exotic shapes. Long, linear edge and hemispherical edge patterns are shown in Fig. 3a and b, respectively. The thickness of the edge regions is about 10 nm or less. The intercalation appears to proceed by a nucleation process, as witnessed by the presence of distinct spheres of varying densities on the edges.

When a graphite plate is held at a slanting plane to the polished electrode surface, different edge planes become visible after intercalation. Such a pattern is presented in Fig. 3c.

3.3.2. Folded graphite plates

One of the main reasons for the improved stability of the polypropylene-graphite composite electrode is the

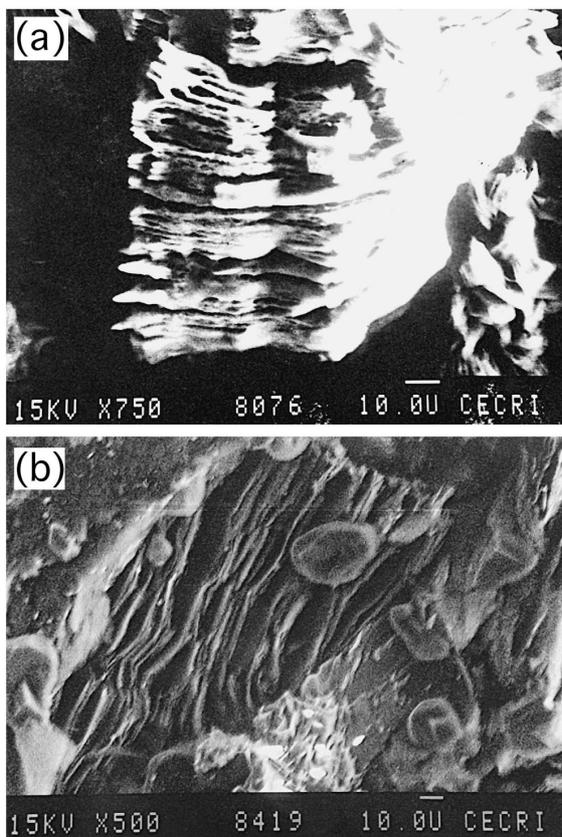


Fig. 5. The scanning electron micrographs of a CPP electrode in 0.25 M solution containing TBAP salt. Intercalation and de-intercalation for 10 min. (a) ClO_4^- intercalated graphite from PC solvent polarized at +2.5 V $\times 750$; (b) TBA^+ de-intercalated graphite from DMSO solvent polarized at -2.5 V and subsequently at -1.4 V $\times 500$.

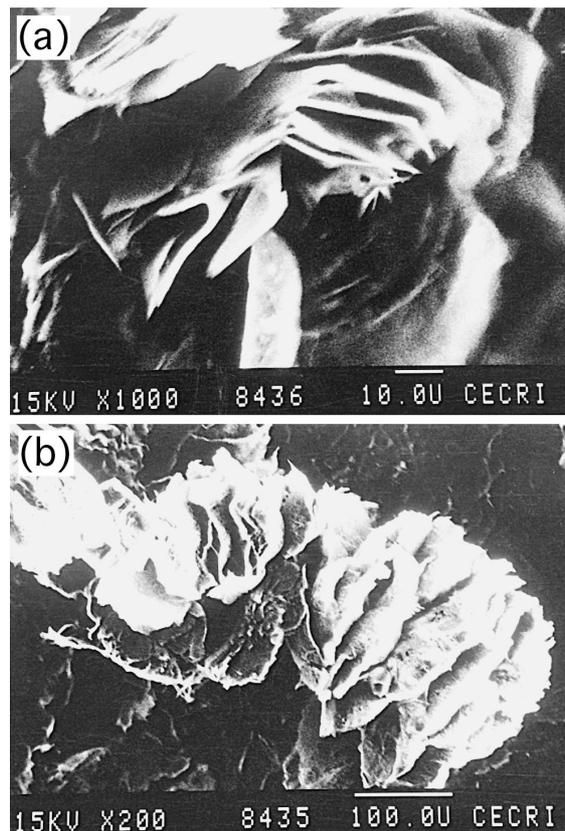


Fig. 6. The scanning electron micrographs of a CPP electrode in 0.25 M AN solution. Intercalation and de-intercalation for 10 min. (a) BF_4^- intercalated graphite polarized at +2.5 V $\times 1000$; (b) ClO_4^- deintercalated graphite polarized at +2.5 V and subsequently at +1.4 V $\times 200$.

strong fixation of graphite plates on the polymer matrix. Nevertheless, these plates, can undergo exfoliation, bending and break down. Some of these features are to be found in Fig. 1a. Fig. 4a shows large graphite plates held strongly in the substrate matrix after Li^+ ion intercalation. Some multi-layered graphite particles can also undergo total folding patterns. Some interesting patterns of this type are presented in Fig. 2b. Uniform folding of a large number of graphite plates after ClO_4^- ion intercalation/de-intercalation in AN media is presented in Fig. 4b.

3.3.3. Multi-layered graphite structure

The CPP electrode is essentially a composite material that contains graphite plates of widely different dimensions together with polypropylene material. The sizes of some of the larger particles may be greater than 200 μm . The edge orientation of these particles is likely to be strongly held and hence exhibit high stability towards intercalation/de-intercalation cycles. This is especially true for multi-layered graphite plates. The micrographs of such edge layers after ClO_4^- anion intercalation in PC and TBA^+ cation intercalation/de-intercalation in DMSO are shown in Fig. 5a and b, respectively. In some regions, the thickness of these plates is appreciable. A portion of such a graphite plate is

shown in Fig. 6a. It is these stable edge planes that impart highly reversible intercalation/de-intercalation behavior and cycling stability to the CPP graphite material.

3.3.4. Special patterns

Fig. 6 presents some unusual microscopic patterns encountered during the present investigations. Even in the randomly held graphite plates, some plates have oriented themselves in a circular fashion (Fig. 6a). This micrograph is indeed quite similar to the micrograph reported earlier for fluoride intercalated carbon fibers [11]. An interesting ‘flower’ pattern which emerges from repeated branches and exfoliated graphite plates is shown in Fig. 6b. These features, however, are not frequently noticed in the micrographic examinations.

4. Conclusions

The present investigations have demonstrated the types of surface transformations that take place on polypropylene-graphite composite material during intercalation and de-intercalation processes. The relationship between surface roughening and IDE is established. During the initial phase of the roughening process, only the horizontally held graphite plates directly exposed to the electrolyte solution are removed. This process leaves behind a more strongly held vertical and slanted graphite plates which also simul-

taneously expose large portions of edge planes for efficient intercalation/de-intercalation. This accounts for the high IDE during multiple cycling. Some interesting micrographic patterns have also been observed during this investigation.

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