

# *Electrochemical behaviour of graphite–epoxy composite materials (GECM) in aqueous salt solutions*

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The electrochemical behaviour of graphite–epoxy composite materials (GECM) in neutral 3.5% aqueous solutions of NaCl has been investigated. Two types of composite and pure graphite have been studied. The composite material shows a high value of electrode potential ranging between  $-40$  and  $+70$  mV versus SCE, and behaves as cathode when coupled to alloys.

The effects of chloride ion concentration, pH, temperature, nature of cations and anions, and resistance of the epoxy matrix to environmental agents on the rate of oxygen reduction reaction on GECM electrodes are reported. Moreover, polarization studies performed on GECM–aluminium alloy couples show that polarization occurs mainly at the composite interface.

From potentiostatic anodic polarization curves of different alloys and cathodic polarization curves of GECM, the initial galvanic corrosion current densities for most alloy–GECM couples of interest in the aerospace industries have been obtained. These values are strongly affected by environment durability of the epoxy matrix and variation by one or two orders of magnitude are observed. Despite the latter discrepancy, these data can be helpful in the assesment of a galvanic series based on galvanic current density for alloy–GECM joints.

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## **1. Introduction**

Recent progress in the field of non-metallic materials in the last decade has highlighted the technological importance of graphite epoxy composite materials (GECM) [1, 2]. GECM are composed of high-strength high-modulus graphite fibres combined with an amine cured polymer epoxy resin. The materials have properties (high strength to weight ratio) such that they offer the possibility of great improvements in the structural efficiency and hence in the operating economics of aircraft.

In such applications, aerospace components made of GECM must be connected to metallic materials. Thus the electrochemical compatibility of GECM with alloys must be taken into account with respect to galvanic corrosion phenomena. Unfortunately GECM behaves electrochemically like a noble metal, showing a high electrode potential which results in an electrical potential difference of about 1V when coupled to aluminium alloys. Because of galvanic corrosion problems, a fundamental consider-

ation in aerospace component design where GECM is one of the proposed materials is the electrochemical compatibility of alloy–GECM joints.

A useful compatibility criterion in galvanic corrosion has recently been pointed out on the basis of average galvanic current density values [3]. In order to obtain such currents both components of the galvanic couple should be electrochemically well defined. While metallic materials have been extensively studied in corrosive environments for many years, GECM has received less attention because of its recent introduction as a substitute for metals. Few papers have appeared in the literature on the electrochemical properties of composite materials [4, 5]. The free corrosion potential, corrosion currents and their variation with different parameters were derived by Brown and Coomber [4] for a class of carbon fibre reinforced plastics (CFRP), while galvanic current densities for alloy–GECM couples have been obtained by Miller [5].

No attention has been paid to the relationship between the composite surface structure and its electrochemical properties despite the significantly large difference in electronic conductivity of the composite components. One of these, i.e. graphite, has been used for many years as an oxygen electrode because of its good electrical properties as well as for the absence of interfering oxide films [6]. Furthermore a possible mechanism for the oxygen reduction on carbon electrodes has been also suggested in which the rate determining step, r.d.s., is the diffusion of oxygen onto the electrode surface [7]. On the other hand, the low electronic conductivity of the polymeric matrix hinders any electrochemical process on its surface. It follows, therefore, that the rate of any electrochemical reaction on GECM is strongly affected by the surface conditions in terms of its composition and structure.

Since the evaluation of the cathodic properties of GECM necessitates the cleaning of its surface with suitable emery paper, there is the possibility of change of structure and composition of the electrode surface. This modification is due to the greater amount of polymeric matrix removed with respect to the graphite fibres in the operation. If this occurs the GECM electrode behaves like a pure carbon electrode and overestimated corrosion currents may be obtained [4]. On the other hand if electrochemical tests are performed on GECM specimens, coming directly from the cure process, then corrosion currents may be underestimated and thus of small interest [5]. Indeed, in practical applications GECMs are covered with suitable sealants in order to minimize the galvanic corrosion arising at the alloy–GECM interface. To increase the adhesion between sealant and composite the latter undergoes a soft surface treatment with emery paper that brings a variation of the composite state surface.

In this paper an attempt is made to clarify the aforementioned aspects by finding a relationship between the surface composition, the free corrosion potentials and corrosion currents. As will be shown in the following, the rate of oxygen reduction on GECM is strongly affected by the amount of material removed from the composite surface.

Finally, the electrochemical behaviour of

GECM from Ciba Geigy and Fiberite having different graphite fibre orientation have been investigated by tracing the potentiostatic cathodic polarization curves in neutral air-stirred 3.5% NaCl solution. The effects of chloride ion concentration, pH, nature of cations and anions and environmental durability on the rate of oxygen reduction on GECM electrodes have also been reported. Moreover, anodic potentiostatic curves for alloys of interest in the aerospace industries are presented, in order to evaluate the initial galvanic corrosion currents for alloy–GECM couples.

## 2. Experimental details

### 2.1. Materials

Metallic materials tested were the aluminium alloys 2024-T3, 7075-T6, 7075-T73, and 5052; stainless steels 301 1/2 H, 302 1/4 H, 321, 15-5-PH, 17-7-PH, 4340 steel and the Ti–6Al–4V and Al–Ni–bronze alloys.

Graphite–epoxy composite materials tested in this study were manufactured by Fiberite and Ciba Geigy and were prepared in the form of square panels by a hand-lay technique and press cured following the cure cycle suggested by the supplier. The relative amount of graphite in the composite was about 60% by volume. In this investigation two different laminates were chosen, namely a unidirectional tape and a woven fabric characterized by a fibre orientation described, according to the notation generally adopted in the appropriate literature, by the sequence: [(0,90)/90/0<sub>2</sub>/±45/0/±45<sub>2</sub>/0/±(45)]<sub>s</sub>. These will be reported as Type 1 and Type 2 throughout the text.

Electrochemical tests were performed on cylindrical specimens of composite material having a thickness of 3 mm and a diameter of 1 cm treated as metallic materials (see below) and on specimens which had not received any surface treatment. The same electrochemical tests were also performed on pure graphite electrodes for comparison.

### 2.2 Test method

The electrolyte used for all tests was 3.3% NaCl

stirred by an air flow of about  $100 \text{ cm}^3 \text{ min}^{-1}$ . The pH of the solution was adjusted to the appropriate value by using HCl or NaOH. All measurements were carried out at a constant temperature of  $25^\circ \text{C}$ .

Before each experiment the surface of the metallic electrode was cleaned with fine emery paper, rinsed in distilled water, degreased in acetone and then dried in an air stream. Cathodic and anodic potentiostatic polarization curves were obtained by following the standard ASTM procedure in an ASTM G5-72 cell by using an Amel (Milan, Italy) potentiostat at a scanning rate of  $40 \text{ mV min}^{-1}$ . A saturated calomel electrode was used as reference.

### 3. Results

#### 3.1. Effect of composite structure

The effect of composite structure on the cathodic behaviour of GECM is shown in Figs 1 and 2 along with the cathodic polarization curve of a

pure graphite electrode. The latter characteristic can be assumed to represent the limiting cathodic behaviour of a GECM electrode.

From the experimental results reported in Fig. 1 (see Curve C), the good electrochemical properties of a graphite electrode for cathodic oxygen reduction are shown. Low overpotentials are required and a high limiting current of about  $200 \mu\text{A cm}^{-2}$  is obtained at a potential value of  $-500 \text{ mV}$ , at which the oxygen reduction reaction is under diffusion control. These results are in agreement with those reported in the literature [8].

Curves A and B of the same figure show the potential-current relationship for Fiberite and Ciba Geigy GECM electrodes having graphite fibres oriented according to the configuration reported in the experimental section. As can be seen the cathodic characteristics of the GECM electrodes differ mainly in the corrosion potential which is  $+72$  and  $+1 \text{ mV}$  respectively. Low current densities (less than  $0.1 \mu\text{A cm}^{-2}$ ) are obtained until a value of  $-250 \text{ mV}$  for the potential is reached. There follows an increase in

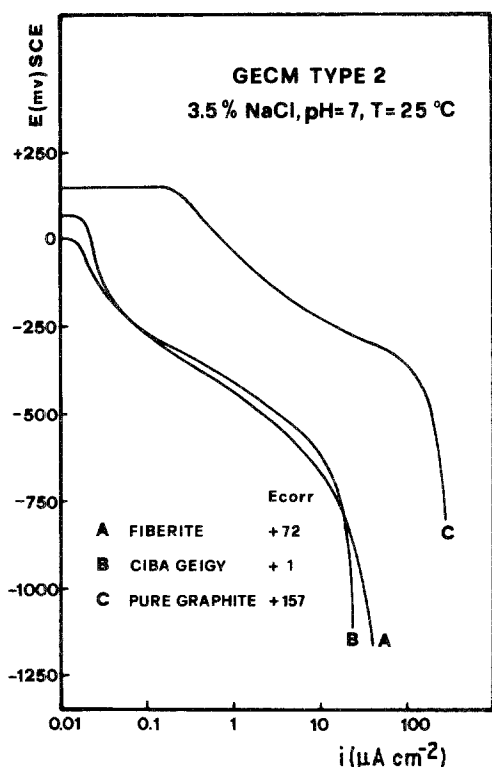


Fig. 1. Potentiostatic cathodic polarization curves of GECM Type 2 in neutral air-stirred 3.5% NaCl.

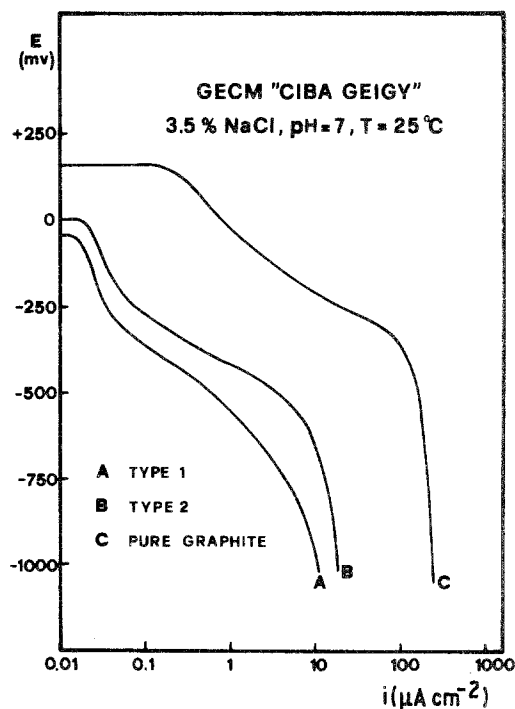


Fig. 2. Effect of graphite fibre orientation on the cathodic behaviour of GECM in neutral air-stirred 3.5% NaCl.

current on lowering the potential and the shape of the curve is similar to that for pure graphite. For all values of electrode potential the currents for the graphite electrode are greater than those observed for GECM electrodes by 1 to 3 orders of magnitude.

The presence of the NH, SO<sub>2</sub>, and OH groups of the epoxy resin may contribute to a change in the double layer configuration and thus the free corrosion potential, while the low electronic conductivity of the polymeric matrix hinders oxygen discharge and thus higher overpotentials are required. Both factors might explain the observed electrochemical differences between GECM and pure graphite electrodes.

The effect of graphite fibre orientation on the cathodic behaviour of GECM is shown in Fig. 2. Currents are greater for the woven composite compared with the directional type at all values of the potential. The observed different electrochemical behaviour can easily be explained on the basis of the greater cathodic area of the former compared with that of the latter composite.

### 3.2. Surface state effect

As far as the oxygen cathodic reaction is concerned GECM can be assumed to be a two-phase electrode having an active cathodic area equal to the exposed surface of graphite fibres and an inert polymeric matrix area. Thus the rate of oxygen reduction is strongly affected by the surface composition or by the amount of graphite exposed to the corrosive environment. In order to find a relationship between the rate of oxygen reduction (corrosion current) and surface composition a systematic investigation of this effect has been carried out and the following results have been obtained.

Firstly it has been found that the main parameter affecting the potential-current relationship is the thickness of material removed rather than the type of emery paper used for the surface treatment. On this basis, the potentiostatic cathodic polarization curves have been traced for GECM electrodes from which 45, 176 and 1721 mg dm<sup>-2</sup> have been removed. Assuming a value of surface density equal to that of the composite (1.4 g cm<sup>-3</sup>), the aforementioned

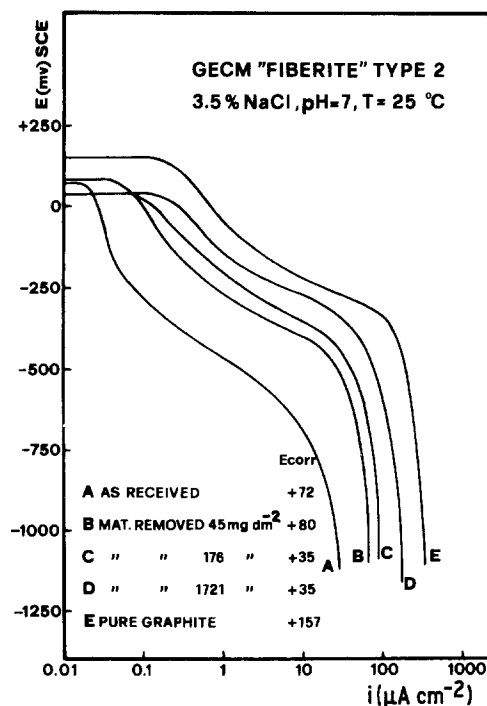


Fig. 3. Effect of material removed on the cathodic behaviour of GECM Type 2 in neutral air-stirred 3.5% NaCl.

amounts give rise to the following thickness of material removed: 3.2, 12.5 and 130  $\mu$ m respectively.

The cathode characteristics of these specimens are reported in Fig. 3 together with those of virgin GECM and that of a pure graphite electrode for comparison. From this figure it appears that:

(a) a thickness of 3  $\mu$ m is sufficient to produce a well defined limiting current for oxygen reduction

(b) the overpotential at the limiting current is, in this case, equal to that of a pure graphite electrode

(c) increasing the thickness of material removed increases the current for each value of the potential

(d) the relative increase in current (based on Curve A) is proportionately less with respect to the amount of material removed

(e) the thickness of material removed does not affect the corrosion potential systematically, at least in the range 3 to 100  $\mu$ m.

(f) by increasing the surface treatment, the cathodic characteristics of a GECM became practically indistinguishable from those of a pure graphite electrode. (These results have not been reported in Fig. 3.)

The results thus obtained clearly indicate that the surface state of a GECM affects the oxygen reduction process and that electrochemical or galvanic data from a GECM electrode must be accompanied by information about the surface treatment used and especially the amount of material removed.

### 3.3. Effect of solution composition, pH and temperature

NaCl concentrations in the range  $10^{-3}$  to 1 M and pH in the range 3 to 11 do not affect the cathodic behaviour of GECM. Moreover, there appears no significant effect on replacing the  $\text{Cl}^-$  anion with  $\text{I}^-$  and  $\text{Br}^-$  or changing the cation from  $\text{Na}^+$  to  $\text{K}^+$ .

The effect of temperature has been investigated by investigating the potentiostatic polarization curves at 25 and 60°C respectively. The results obtained show an increase in corrosion currents of about 3% per °C rise in temperature which agrees with literature results on the kinetics of oxygen reduction in aerated water [9].

### 3.4. Effect of environment durability

It is well known that composite materials made of epoxy resin, suffer a degradation process owing to the dissolution and diffusion of water in the polymeric phase. Chemical and physical degradation induced by water, may be so pronounced as to affect the mechanical properties of the composite material [10, 11].

In this section attention is focused on a different aspect of the aforementioned sorption process, namely on the relationship between environment durability and electrochemical properties such as corrosion potential and cathodic behaviour. Three GECM specimens of Ciba Geigy Type 1 (i.e. unidirectional tapes) were exposed to different environments and the potentiostatic polarization curves were traced in 3.5% NaCl.

The results obtained are reported in Fig. 4. as

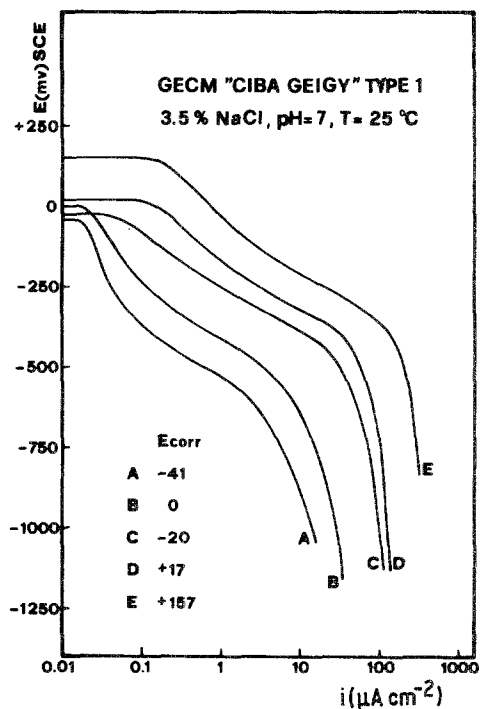


Fig. 4. Effect of environment on the cathodic behaviour of GECM Type 1 in neutral air-stirred 3.5% NaCl. Curves A to E refer to the following conditions: A: virgin GECM, B: GECM exposed to distilled water for 5 months, C: shadow-side of a GECM exposed to the atmosphere in the Naples area for 15 months, D: sun-side of a GECM exposed to the atmosphere in the Naples area for 15 months.

Curves B, C and D. In the same figure the cathodic characteristics of a virgin GECM (Curve A), and of a pure graphite electrode (Curve E) are also reported.

The cathode curve B is for a GECM specimen immersed in distilled water at 25°C for 5 months. In this case the amount of water sorbed is equal to 2% by weight. This value represents saturation for the given specimen size. Curves C and D refer to the shadow surface side and to sun surface side of two specimens exposed to the atmosphere for 15 months in the Naples area.

Microscopic observation of these surfaces shows the presence of local swelling, uncovered graphite fibres and of micro- and macro-cavities.

The results of Fig. 4 can be explained on the basis of the following arguments. The water sorbed by specimen B induces a physical separation between the polymeric matrix and the

graphite fibres which leads to an increase of effective cathodic area. Indeed the shape of Curve B is similar to that of Curve A.

The cathodic behaviour of GECM exposed to the atmosphere is quite different as can be seen from Fig. 4. Higher values of corrosion current and low overpotential are observed, which make these similar in shape to that for a pure graphite electrode. These results can be explained on the basis of a concomitant action of many factors such as: chemical degradation of the polymeric matrix induced by UV radiation, residual stress due to thermal gradients, water adsorption, removal of damaged resin by rain and synergic effects. As a consequence there is a large increase in the exposed area of graphite fibre compared to that of a virgin GECM.

These results are of importance in aerospace component design since they clearly indicate the variation of electrochemical properties of GECM induced by different environments.

Moreover it is observed that the cathodic characteristic such as those of Curves B, C and D are similar to those reported in Fig. 3. This similarity furnishes an alternative procedure for evaluating long-term electrochemical properties by performing suitable equivalent short-run tests. Further studies are in progress in order to give a greater understanding of the role played by the sorbed water on the observed cathodic time behaviour of GECM.

### 3.5. Potentiostatic polarization curves of uncoupled alloy and galvanic couples

Potentiostatic anodic polarization curves for uncoupled aluminium alloys 2024-T3, 7075-T6, 7075-T73 and 5052; stainless steels 301 1/2 H, 302 1/4 H, 321, 15-5-PH, 17-7-PH, 4340 steel and the Ti-6Al-4V and Al-Ni-bronze alloys have been performed in order to evaluate the initial galvanic current density according to the procedure reported in the literature [12].

The initial galvanic current is the current at the intersection of the cathodic polarization curve of the cathode (GECM) and the anodic polarization curve of the anode (metallic alloy). In Fig. 5 the results relative to the couples 2024-T3-GECM and 7075-T6-GECM are reported.

The cathodic curves reported are referred to

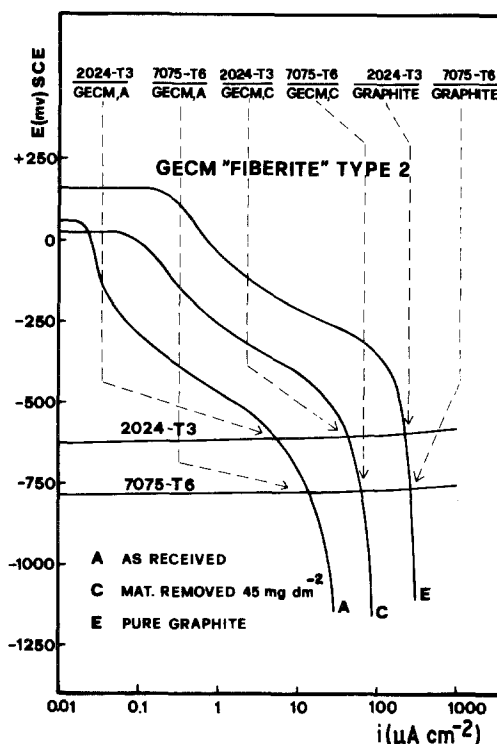


Fig. 5. Cathodic branch of potentiostatic polarization curves for virgin GECM (Curve A), for a surface treated GECM (Curve C) and for a pure graphite electrode (Curve E) superimposed on potentiostatic anodic polarization curves for aluminium alloys in neutral air-stirred 3.5% NaCl.

a virgin GECM (Curve A) and to a GECM treated surface (Curve C) and to a pure graphite (Curve E). The galvanic currents are indicated by arrows and it can be seen that they are strongly affected by the state of the surface. In the same figure the currents relative to the alloy-graphite couples are also reported for comparison since they are the maximum galvanic currents allowed for alloy-GECM joints. The values thus obtained are collected in Table 1.  $i_{go,0}$ ,  $i_{go,1}$  and  $i_{go,L}$  are respectively the initial galvanic current densities in  $\mu\text{A cm}^{-2}$  obtained by coupling a virgin GECM, a surface treated GECM and pure graphite to the alloy reported in the first column.

By comparing the values of  $i_{go,0}$  and  $i_{go,1}$ , it is clearly seen that the surface treatment affects the galvanic current by one order of magnitude for most of the investigated alloys despite the small thickness of materials removed which, as already mentioned, is about  $3 \mu\text{m}$ . On the other

Table 1. GECM Fiberite type woven fabric coupled with:

	$i_{go,0}$ ( $\mu\text{A cm}^{-2}$ )	$i_{go,1}$ ( $\mu\text{A cm}^{-2}$ )	$i_{go,L}$ ( $\mu\text{A cm}^{-2}$ )
302 1/4 H	0.1	1	2
17-7-PH	0.4	0.6	1
301 1/2 H	0.1	0.8	1.5
Al-Ni-bronze	0.1	2	10
15-5-PH	0.7	0.7	1
321	0.2	2	3
Ti-6Al-4V	0.2	1	1.5
4340	3	40	200
2024-T3	5	45	200
5052	16	75	250
7075-T73	17	70	250
7075-T6	13	70	250

Initial galvanic current densities in  $\mu\text{A cm}^{-2}$  for alloy-GECM couples in neutral air-stirred 3.5% NaCl.  $i_{go,0}$ ,  $i_{go,1}$ ,  $i_{go,L}$  are the initial galvanic current densities obtained by coupling a virgin GECM, a surface treated GECM and pure graphite to the alloy reported in the first column. The cathodic to anodic area ratio is 1.

hand a thickness of 3  $\mu\text{m}$  can be easily removed in industrial applications of such composites.

Thus it may be questionable whether or not a virgin GECM should be used, rather than a slightly treated GECM, in order to obtain a more realistic galvanic series based on galvanic current densities [5]. Moreover only on the basis of suitable series can an appropriate compatibility criterion based on the average galvanic current densities be derived.

Appropriate values of galvanic currents are also useful in assessing the type and amount of primer to be used in order to avoid electrical contact between GECM and alloy in a working structure.

The authors are fully aware of the preliminary character of the above results. Accordingly, the extension of this work to the study of galvanic corrosion at the GECM-alloy interface will be carried out on the basis of direct measurement of galvanic currents which, accounting for polarization phenomena, should give values of current densities less than  $i_{go,0}$ . This aspect will be dealt with in subsequent papers.

#### 4. Conclusions

From the results reported in this paper, the following main conclusions can be drawn:

(a) No significant difference was found between the electrochemical cathodic behaviour of GECM from Ciba Geigy and from Fiberite in neutral aqueous solution of NaCl. A small difference was observed in the behaviour of unidirectional tapes and woven fabric types from the same supplier.

(b) The rate of cathodic oxygen reduction in neutral aqueous solutions of NaCl on GECM electrodes is strongly affected by the surface state of the composite. An increase of the amount of material removed from the surface increases the corrosion current.

(c) pH variation in the range 3 to 11, salt concentration in the range  $10^{-3}$  to 1M and nature of anions and cations have small effects on the cathodic behaviour of GECM.

(d) Variation of corrosion currents by one order of magnitude may occur when the epoxy adhesion capability decreases due to adsorbed water. There follows an increase in the effective graphite fibre cathodic area for oxygen reduction and thus higher corrosion currents are observed. This effect is further complicated by chemical epoxy degradation due to UV radiation.

(e) Finally, galvanic corrosion currents have been obtained via potentiostatic polarization curves. These currents appear strongly dependent on the surface treatment of the GECM and variation of one order of magnitude for small thicknesses of surface material removed have been observed.

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