Carbon fiber reinforced polymer (CFRP) has found many applications in infrastructure construction, automobile, aircraft and aerospace industries due to its light weight, high stiffness, high strength, good anti-fatigue performance and excellent corrosion resistance. Many investigators have been attracted to pursue better mechanical properties for different types of CFRPs. CFRPs are often used together with other engineering metals, such as steels, Al alloys, Mg alloys and Ti alloys in industry. As carbon has an open-circuit-potential (OCP) more positive than most engineering metals, strong galvanic cells can be formed between CFRPs and these metals in aggressive service environments. Thus galvanic corrosion of the coupled metals has been always a big concern. In the past decades, many studies have been focused on the galvanic effect of CFRPs on the coupled metals, including the influence of metallurgical and environmental factors on the galvanic corrosion. These have led to some common knowledge. For example, it has been generally accepted that, apart from the well-known galvanic corrosion of steels caused by CFRPs, aluminum alloys with good general corrosion resistance, can also suffer from galvanic corrosion if they are coupled with CFRPs. The galvanic corrosion of magnesium alloys coupled with CFRPs is more severe than any other engineering metals. Titanium alloys are stable in most aggressive environments and not attacked by galvanic corrosion if they are in contact with CFRPs.

However, most of these studies simply measured or estimated the corrosion damage of metals. They ignored the detailed electrochemical behavior of the coupled CFRPs. In fact, the metal in contact with a CFRP may deteriorate more severely due to crevices formed in the joint that simply caused by galvanic effect. On the other hand, the CFRP in a galvanic couple may also degrade and its electrochemical properties may vary with time while the coupled metal is being corroded, as the corrosion products from the coupled metal may in return affect the electrochemical performance or even accelerate the degradation of the CFRP. This kind of possible degradation of a CFRP in a galvanic couple, as well as the detrimental effect of the CFRP degradation on the galvanic corrosion of a coupled metal, has not been systematically investigated.

In fact, CFRP can degrade in a corrosive medium chemically and physically. The chemical degradation is an irreversible fracture of chemical bonds, while the physical damage normally initiates from diffusion of the corrosive medium into the composite. Both are more likely to occur under an immersion condition. Since an electrochemical reaction can alter the chemical and physical states at the interface between ionic (water present in polymer defects) and electronic (carbon fiber) conductors, there is the likelihood of electrochemical polarization will further accelerate the degradation of CFRP. In fact, strong polarization may occur on a CFRP component in practical applications. For example, stray currents may be generated around a cathodic protection system in an underground, submarine or continuous wetting condition. These currents may flow in and out of a CFRP part, resulting in strong cathodic and anodic polarization on the CFRP if the CFRP is not electrically connected to another metal or earth ground. However, this inference currently is only a conjecture due to lack of direct experimental evidence. Although a polymer has been reported to break down on a cathodic surface and a CFRP has been found to degrade more rapidly in a NaOH solution or in a simulated pore solution of concrete in a cathodic protection system or under an oxygen evolution condition, no research effort has been made to verify the effect of electrochemical polarization on the CFRP degradation.

Since the electrochemical performance of a CFRP in theory has a significant influence on the galvanic corrosion of a coupled metal and the degradation of the CFRP can be affected by electrochemical reactions on its surface, a detailed study on the electrochemical behavior of the CFRP will be of great importance. It concerns not only the scientific understanding, but also the practical application of the CFRP.

In a CFRP composite, the carbon fiber reinforcement is electrochemically active, while the polymer matrix is inert, and the surface polymer layer can critically influence the electrochemical behavior of a CFRP. Therefore, in this study, the influence of CFRP composite microstructure, particularly the surface polymer layer, on the electrochemical behavior of the CFRP was investigated. The goal of this study is to better understand the electrochemical behavior of CFRPs and further extend their applications in industry.

Materials and Methods

Materials and solutions.—Considering existing applications of CFRP in the auto industry, the GMW14872 standard solution, 0.9 wt% NaCl + 0.1 wt% CaCl₂ + 0.075 wt% NaHCO₃, was selected as a standard test solution in the study. In addition to the standard electrolyte, neutral demineralized water, HCl solutions and NaOH solutions with different pH values (2, 4, 6, 8, 10 and 12) were also used in immersion tests. All the solutions were prepared with a neutral demineralized water that had conductivity ~10μS/cm and analytical grade chemicals.
Table I. Constituents of the carbon fiber reinforced polymers.

| Sample   | Component                                      |
|----------|------------------------------------------------|
| E-CFRP   | 57 vol.% carbon fiber in epoxy (fabricated at GM R&D) |
| T-CFRP   | 45 vol.% carbon fiber in nylon 6,6 (200 g/m² fabric) |

(Bond Laminates TEPEX Dynalite 201-C200(6))

Two types of carbon fiber reinforced polymer sheets named E-CFRP and T-CFRP were used. The E-CFRP sheets were constituted of carbon fiber and epoxy, while the T-CFRP samples were carbon fiber reinforced nylon. The compositions of these two CFRPs are listed in Table I. The CFRP sheets were cut into 10 cm × 4 cm × 1.6 mm coupons. A hole 1 cm in diameter was drilled in them (for screw joining purpose). Before tests, all the coupons were ultrasonically cleaned in deionized water and then dried in air.

To observe the microstructures of the CFRPs, their polymer surface layers were removed by grinding using 80 grit sandpaper. The thickness of removed surface layers was about 0.05 mm. The cross-sections of the CFRPs were observed from the edges of these coupons.

**Electrochemical measurements.**—According to a previous study, CFRPs have good bulk conductivity. Thus, traditional electrochemical measurements can be carried out on them directly. An electrochemical workstation AUTOLAB (PGSTAT302) was used for electrochemical tests, and the measurements were conducted in a three-electrode electrolyte cell containing 100 ml of the GMW14872 standard solution. This cell allowed a CFRP sample as working electrode to attach from the outside and to expose a 0.78 cm² surface area to the electrolyte inside. The counter electrode in the cell was a platinum foil and the reference between the counter and working electrode in the cell was a saturated Ag/AgCl/KCl electrode.

EIS measurements were carried out at the OCP of the measured CFRP. The AC potential amplitude was 10 mV and the frequencies ranged from 1 mHz to 100 kHz with 10 frequency points in a logarithmic decade. The CFRP sample was exposed to the solution for 1200s~1300s before EIS measurement each time. In polarization curve measurements, the potentiodynamic scanning rate was 1 mV/s and scanning range −3 V~+3 V (vs. OCP). Potentiostatic polarization measurements were also conducted on the CFRP samples at ±1V, ±2V, ±3V vs. OCP.

**Immersion test.**—The CFRP samples were also immersed in the neutral deionized water (pH 7), NaOH and HCl solutions with different pH values for 5 days. Their morphological changes were examined after immersion.

**Microstructure characterization.**—Using a BioLogic M470 Scan Electrochemical Workstation, an optical surface profilometry (OSP) technique was employed to characterize the surface morphologies of the CFRPs. The optical surface profilometry (OSP) photos (see Figure 2) shows the micro-morphologies and cross-section microstructures of the CFRPs were also obtained by Scanning Electron Microscopy (SEM, SU70 Hitachi and TM3000), in which the accelerating voltage was 5 kV, deceleration voltage 0 V and emission current 48 μA. The surface micro-morphologies and cross-section microstructures of the CFRPs were also obtained by Scanning Electron Microscopy (SEM, SU70 Hitachi and TM3000), in which the accelerating voltage was 5 kV, deceleration voltage 0 V and emission current 48 μA.

The surfaces of the CFRP coupons were observed before, after and in situ in the standard test electrolyte at different voltages and in the deionized water and the solutions with different pH values at their OCPs under a Leica microscope.

**Results**

**Surface morphologies.**—Figure 1 shows the morphologies of the two types of CFRPs before and after surface grinding. The patterns on their surfaces are different. On the front surface of the E-CFRP there are zig-zag (+45° and −45°) lines between two longitudinally parallel lines, while on the back surface the lines perpendicularly cross each other (Figure 1a). Throughout the front and back surfaces of the E-CFRP, the bundle patterns are perpendicularly knitted like a “woven bag” (Figure 1b). The ground surfaces are also shown in Figures 1c and 1d. Both the front and back surfaces of the E-CFRP sample after grinding are full of +45° and −45° line patterns in addition to some blurred horizontal and vertical lines (Figure 1c). On the T-CFRP surface, the perpendicularly knitted bundle pattern throughout the front and back surfaces remains unchanged after surface grinding (Figure 1d). These suggest that the texture patterns originally on the E-CFRP and T-CFRP surfaces do result from the different distributions of the carbon fiber bundles in these two CFRPs.

The optical surface profilometry (OSP) photos (see Figure 2) shows that the area with a carbon fiber bundle underneath is slightly higher than the area without a carbon fiber bundle underneath on the original surface. Some small areas with a gap between carbon bundles sink deeply into the CFRP bulk, as pointed out by the arrows in the figure. Surface grinding removed the surface polymer layer. This explains the ground E-CFRP surfaces dominated by different textures (Figures 2a and 2b). The unchanged texture of T-CFRP after surface grinding suggests that the carbon fiber bundles underneath the surface polymer layer are similarly knitted (Figure 2c). The surface of T-CFRP is smoother than that of E-CFRP (Figures 2a, 2b and 2c).

The surface micro-morphologies of the CFRPs are shown in Figure 3. No carbon fiber is exposed on the E-CFRP surface, but some tiny dents in the surface epoxy layer (Figure 3a). The carbon fiber bundles in the E-CFRP sample are revealed after surface grinding (Figure 3b). On the T-CFRP surface (Figure 3c), the carbon fiber bundle texture can be clearly seen under SEM in some areas before surface grinding, indicating that the surface nylon layer over the carbon fiber is very thin or even broken (cannot conceal the carbon fiber bundles) in some areas. Surface grinding resulted in complete exposure of carbon fibers (Figure 3d).

**Composite structures.**—The layer structures (which have been confirmed by the suppliers) of the E-CFRP and T-CFRP are schematically illustrated in Figure 4. The E-CFRP consists of 8 layers of carbon bundles, laying at 0°/45°/−45°/90°/90°/−45°/45°/0°, layer by layer from the top to the bottom, while the T-CFRP has 6 layers and...
in each layer the carbon bundles in $0^\circ$ and $90^\circ$ directions are woven together. It should be noted that each of the bundles contains many carbon fiber filaments.

The SEM cross-section images of these two types of CFRPs (Figure 5) confirm that the E-CFRP is like a “sandwich” with different directions of carbon fiber bundles in different layers (Figure 5a) and between carbon fiber bundles there are some gaps not filled by epoxy resin, while the fiber bundles (those in different directions having color contrast) in the T-CFRP are “woven” (vertically overlapped) together in the same layer (Figure 5b). The carbon fiber filaments have a clean surface, not covered by epoxy resin at the edges (Figure 5c). The gaps between polymer and carbon fiber filaments in the E-CFRP can also be visualized there. In contrast, the carbon fiber filaments are well buried in nylon even at the edges (Figure 5d), and no gap is formed between carbon fibers and polymer in the T-CFRP (Figure 5b).

Figure 6 shows surface polymer layers over carbon fibers in E-CFRP and T-CFRP. The surface polymer layer on the E-CFRP is about 6 $\mu$m thick. The carbon fiber filaments are about 5 $\mu$m in diameter. For T-CFRP, this surface layer is very thin, which is difficult to distinguish. In many areas the carbon fibers may directly be exposed without a surface nylon layer covering them.
Figure 4. Illustration of the layered structures of (a) E-CFRP, (b) T-CFRP, and (c) the cross-section of a carbon fiber bundle containing carbon fiber lines.

Figure 5. Cross-section SEM images of CFRPs: (a) carbon fiber bundle layers in E-CFRP, (b) carbon fiber bundle layers in T-CFRP, (c) carbon fiber exposed at the edge of the E-CFRP coupon, (d) carbon fiber exposed at the edge of the T-CFRP coupon.

**Electrochemical characteristics.**—The potentiodynamic polarization curves of the two types of CFRPs before and after surface grinding are shown in Figure 7. The T-CFRP has a slightly more positive open-circuit potential ($E_{ocp}$) than the E-CFRP. The polarization current densities of T-CFRP are higher than those of E-CFRP in the potential range from $-3\text{V}$ to $+2\text{V}$ vs. Ag/AgCl, and the differences become insignificant with increasing potential. On the polarization curve of E-CFRP, there are two transition points: $+1.55\text{V}$ and $-2.03\text{V}$ (vs. Ag/AgCl). Similarly, the two transition points on the polarization curve of T-CFRP are at $+1.89\text{V}$ and $-1.88\text{V}$ (vs. Ag/AgCl). At these transition points, the current densities suddenly change. After surface grinding, both the anodic and cathodic polarization current densities of the two kinds of CFRPs dramatically increase. Their polarization curves are almost overlapped each other, and their OCPs (or $E_{corr}$) become more negative. Both the CFRPs after surface grinding have two transition points at $+1.04\text{V}$ and $-1.38\text{V}$ (vs. Ag/AgCl) at their anodic and cathodic polarization curves, respectively. The similarity in polarization behavior for the E-CFRP and T-CFRP after surface grinding obviously results from the exposure of carbon fiber bundles. Since the carbon fiber bundles in the E-CFRP and T-CFRP have the same electrochemical behavior in the electrolyte, the differences in polarization behavior between the unground and ground samples should be caused by the different surface polymer layers on the E-CFRP and T-CFRP.

The typical EIS measurements for E-CFRP and T-CFRP samples measured at their OCPs are presented in Figure 8, which show the impedance behavior of the surface polymer layers on the E-CFRP and T-CFRP. The reproducibility of the EIS measurements on the E-CFRP samples is much worse than that on the T-CFRP. The electrochemical impedance spectra of the T-CFRP have a Warburg diffusion characteristic, while those of the E-CFRP do not. The resistance of the E-CFRP estimated from the EIS measurements is much larger than that of the T-CFRP.

Simple equivalent circuits as shown in Figures 8a and 8b are employed to fit the measured electrochemical impedance spectra of the E-CFRP and T-CFRP, respectively, in order to estimate the resistance ($R$) of the surface polymer layer, the solution resistance ($R_s$) between the reference electrode and the CFRP surface, the distributed capacitance ($Q$) of the surface polymer layer, and the Warburg...
impedance ($Z_w$) for oxygen diffusion in water through defects in the surface layer for these two CFRPs. No $Z_w$ is involved in the simple equivalent (Figure 8a) in fitting the E-CFRP impedance spectra, while $Z_w$ is an essential important component in the diffusion controlled equivalent circuit (Figure 8b) to better fit the T-CFRP EIS results. The distributed capacitance $Q$ refers to the total capacitance ($C$) of all the micro-pores distributed throughout the surface polymer layer. Due to the imperfect capacitance behavior, $Q$ normally acts like a constant phase element (CPE). To better fit the measured EIS results, $Q$ instead of $C$ is used in the equivalent circuit and the curve-fitted $Q$ values are listed in Tables II and III. $Q$ can be converted to $C$ through the Brug approach.43 The converted $C$ values are also listed in Tables II and III, and will be discussed later. In Table II both E-CFRP and T-CFRP have a high surface layer resistance, but in average the former ($1.35 \times 10^7$ Ω·cm²) is nearly 3 orders of magnitude higher than the latter ($4.26 \times 10^4$ Ω·cm²), suggesting that the former surface can be more completely covered by an electrically insulating layer, whereas the surface layer on the latter may contain more defects in which the carbon fiber bundles can be exposed to the solution in some areas.

Figure 8 presents impedance spectra of the two types of CFRPs after surface grinding. The simple equivalent circuit as shown in Figure 9 was used to estimate the electrochemical parameters of the surface ground CFRPs, and their estimated results are listed in Table III. The results can be summarized as follows: (1) The resistance of the E-CFRP is reduced dramatically after surface grinding, while the resistance reduction for the T-CFRP is not so evident. The reproducibility of the EIS measurements on the surface ground E-CFRP

| Table II. Surface polymer layer resistance ($R$), capacitance ($C$) and Warburg diffusion impedance ($W$) for the E-CFRP and T-CFRP. |
| Sample | E-CFRP $R$ (Ω·c㎡) | E-CFRP $Q$ (Mho·S) | E-CFRP $C$ (F·c㎡) | T-CFRP $R$ (Ω·c㎡) | T-CFRP $Q$ (Mho·S) | T-CFRP $C$ (F·c㎡) | T-CFRP $W$ (Mho·S)$^{1/2}$ |
|--------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 1      | 8.30 x 10^4     | 7.46 x 10^{-9}  | 3.00 x 10^{-9}  | 2.74 x 10^{-8}  | 8.36 x 10^{-8}  | 1.52 x 10^{-8}  | 7.65 x 10^{-6}  |
| 2      | 6.46 x 10^7     | 1.83 x 10^{-8}  | 1.92 x 10^{-8}  | 8.56 x 10^{-6}  | 6.43 x 10^{-8}  | 1.46 x 10^{-8}  | 5.31 x 10^{-6}  |
| 3      | 1.60 x 10^8     | 1.09 x 10^{-8}  | 1.21 x 10^{-8}  | 1.07 x 10^{-6}  | 1.27 x 10^{-7}  | 2.63 x 10^{-8}  | 5.04 x 10^{-6}  |
| 4      | 2.26 x 10^8     | 8.75 x 10^{-9}  | 9.57 x 10^{-9}  | 3.17 x 10^{-6}  | 1.27 x 10^{-7}  | 2.33 x 10^{-8}  | 5.47 x 10^{-6}  |
| 5      | 5.98 x 10^1     | 1.10 x 10^{-8}  | 1.51 x 10^{-8}  | 5.78 x 10^{-6}  | 6.57 x 10^{-6}  | 1.19 x 10^{-8}  | 5.06 x 10^{-6}  |
| Average | 9.03 x 10^7     | 1.18 x 10^{-8}  | 4.26 x 10^{-8}  | 1.83 x 10^{-8}  | 7.51 x 10^{-6}  | 5.54 x 10^{-9}  | 9.85 x 10^{-7}  |
| Standard deviation | 8.95 x 10^7     | 5.44 x 10^{-9}  | 2.63 x 10^{-6}  | 5.54 x 10^{-9}  | 9.85 x 10^{-7}  |

| Table III. Surface resistance ($R$) and capacitance ($C$) of the E-CFRP and T-CFRP after removal of their surface polymer layers by grinding. |
| Sample | E-CFRP $R$ (Ω·c㎡) | E-CFRP $Q$ (Mho·S) | E-CFRP $C$ (F·c㎡) | T-CFRP $R$ (Ω·c㎡) | T-CFRP $Q$ (Mho·S) | T-CFRP $C$ (F·c㎡) |
|--------|------------------|------------------|------------------|------------------|------------------|------------------|
| 1      | 5.05 x 10^4     | 2.06 x 10^{-5}  | 2.29 x 10^{-5}  | 2.41 x 10^{-4}  | 2.50 x 10^{-5}  | 2.99 x 10^{-5}  |
| 2      | 9.77 x 10^5     | 2.02 x 10^{-5}  | 2.53 x 10^{-5}  | 1.15 x 10^{-4}  | 6.20 x 10^{-5}  | 8.34 x 10^{-5}  |
| 3      | 5.42 x 10^4     | 3.27 x 10^{-5}  | 3.79 x 10^{-5}  | 1.21 x 10^{-4}  | 6.66 x 10^{-5}  | 7.20 x 10^{-5}  |
| Average | 6.75 x 10^4     | 2.87 x 10^{-5}  | 1.59 x 10^{-4}  | 6.18 x 10^{-5}  | 2.30 x 10^{-5}  |
| Standard deviation | 2.14 x 10^4     | 6.58 x 10^{-6}  | 5.80 x 10^{-3}  |
samples is improved significantly. (2) After surface grinding, the resistance values of the E-CFRP and T-CFRP samples are in the same order of magnitude and the resistance reduction by surface grinding is more significant for E-CFRP than for T-CFRP. (3) The Warburg diffusion characteristics of the T-CFRP disappear after its surface is ground. These differences in EIS further confirm that surface epoxy layer on the E-CFRP is more resistant or contain fewer defects than the surface nylon layer on the T-CFRP. Nevertheless, the resistance of the ground E-CFRP is still over 3 times larger than that of the ground T-CFRP, and the capacitance of the former is only half of the latter. These can be attributed to the different amounts and distributions of the carbon fiber bundles in these two CFRPs. According to the composite structure, the polarization resistance of the outermost carbon fiber bundle layer in the ground E-CFRP is $\sim 1.8 \times (1.2/(2/3))$ times (significantly) higher than that in the T-CFRP, and the capacitance of the former should be much smaller than that of the latter.

**Polarization damage.**—The surface morphologies of the CFRPs after polarization at different anodic and cathodic potentials are shown in Figures 10, 11 and 12. Polarization voltages $\pm 1\text{V}$ (vs. OCP) cannot significantly change the surface morphologies of the CFRPs (Figure 10). When the voltages reach $\pm 2\text{V}$ (vs. OCP), the change becomes obvious; the surface polymer layer of E-CFRP breaks into pieces and falls off, and the underneath carbon fiber bundles are exposed (Figure 11). Surface layer damage can also be observed on the E-CFRP after polarization at $-2\text{V}$ (vs. OCP) for 2h. The damage of the surface layer on the T-CFRP at $+2\text{V}$ and $-2\text{V}$ (vs. OCP) is slightly less serious than that of the E-CFRP at the same polarization potential. The surface polymer layer in the damaged area on the T-CFRP at $+2\text{V}$ (vs. OCP) appears to be torn-off, and the carbon fiber bundles can be clearly seen there. After polarization at $-2\text{V}$ (vs. OCP), the surface layer of the T-CFRP is like a paste stuck on the fibers. When the polarization potential reach $\pm 3\text{V}$ (vs. OCP), the surface polymer layer damage is so severe that can even be visualized by the naked eye (Figure 12). Overall, the damage on the E-CFRP is more serious than on the T-CFRP under all the polarization conditions. Moreover, the damage on the E-CFRP caused by strong polarization is randomly distributed, whereas that on the T-CFRP has a pattern similar to the distribution of the underneath carbon fiber bundles.

Figure 13 shows gas bubbles on the CFRP surfaces polarized at $3\text{V}$ vs. OCP in the standard test electrolyte. The bubbles generated at some points on both the E-CFRP and T-CFRP grew quickly there. After the bubbles were released, some damaged areas on the E-CFRP surfaces became evidently visible. T-CFRP also had similar surface
Figure 12. Surface morphologies of the E-CFRP and T-CFRP after 2 hours of polarization at voltage ±3V vs. OCP. (a) Enlarged damaged area from (b), (b) E-CFRP polarized at +3V vs. OCP, (c) E-CFRP polarized at −3V vs. OCP, (d) enlarged damaged area from (e), (e) T-CFRP polarized at +3V vs. OCP, and (f) T-CFRP polarized at −3V.

Figure 13. Gas bubble generating and releasing with time on the E-CFRP and T-CFRP surfaces at +3V vs. OCP: (a) E-CFRP, (b) T-CFRP.

Discussion

Surface polymer layer model.—The penetration of water/electrolyte through a polymer layer can be divided into three stages: (1) the electrolyte enters the polymer, (2) the entered solution reaches the carbon fiber, and (3) the amount of the solution in the polymer and at the interface of polymer/carbon fiber gradually increases, and the polymer matrix becomes more conductive with time.44 The microstructure of the surface polymer layer of a CFRP can significantly influence the solution ingress and the electrochemical behavior of the CFRP.

According to the composition (Table 1), surface morphology (Figures 1, 2 and 3), microstructure (Figures 4 and 5) and the surface layer (Figure 6) results, a model for the surface structures of the two kinds of CFRP is proposed and schematically illustrated in Figure 15. There are three types of surfaces under different conditions: original surface (OS), electrochemical reaction surface (ES), and polished surface (PS). The model has 5 important characteristics: (1) the surface polymer layer of E-CFRP is thicker than that of T-CFRP, (2) the surface of T-CFRP is more uniform than that of E-CFRP, (3) there are fewer defects on the surface layer of E-CFRP than T-CFRP surface, (4) more gaps are formed at the interfaces between carbon fiber bundles and the polymer in E-CFRP than in T-CFRP, and (5) some defects penetrate through the surface polymer layer and the carbon fiber can be exposed to solution through them, while the others are not.

It should be noted that even in some carbon fiber-visible areas, the carbon fiber bundles are actually not directly exposed. Figure 3c shows that at least 1/4 of the T-CFRP surface is carbon fiber-visible. If carbon fiber bundles in these areas were all directly exposed, then measured polarization current densities would be much higher, close to those of the ground T-CFRP. However, the experimental results (see Figure 7) indicate that the polarization current densities around the OCP for T-CFRP are 1 order of magnitude lower than those of the ground T-CFRP. This implies that there is still a porous thin (transparent) polymer film over the visible carbon fiber bundles. Thus, the effective defect area (where the carbon fiber is directly exposed) is actually much smaller than the carbon fiber-visible area (apparent defect area) on the original surface.

The microstructure model (Figure 15) is valid during the whole experimental period, even after a long-term immersion. Theoretically, solution cannot get into a defect not connected to the surface, and thus such a defect will not affect the electrochemical performance. However, in practice the cross-linking among polymer molecules and the bonding between carbon fiber and polymer matrix may break down after long-term immersion (perhaps over months). Hence, the porosity and the number of effective defects may gradually increase, and solution may travel along the carbon fiber-polymer interface. Consequently, and the resistance and capacitance of the CFRP may slowly decrease and increase with time, respectively.

Electrochemical behavior.—It is clearly shown in Figure 7 that the current densities of T-CFRP are higher than those of E-CFRP
under polarization. This is obviously caused by the different surface polymer layers of these two CFRPs and the defects in them. On the T-CFRP, there are more defects in the thin surface polymer layer, and water can reach the carbon fiber more easily than on the E-CFRP. Thus, through so many defects, the polarization current densities can reach much higher levels at different potentials on the T-CFRP than on the E-CFRP.

When the surface layer is removed, the electrochemical performance will purely be dependent on the exposed carbon fiber, and the polarization current densities will be determined by the number or the total surface area of the directly exposed carbon fiber bundles. In this case, the E-CFRP and T-CFRP will have almost the same current densities.

There are always transition points on the polarization curves of the unground and ground CFRPs. The transition points on the anodic and cathodic polarization curves of the ground CFRPs correspond to oxygen generation $4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ and hydrogen evolution $2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^-$ respectively, as gas bubbles were observed on the sample surfaces under these conditions.

These reactions should also be responsible for the sudden current density increases (transition points) on the polarization curves of the unground CFRPs. Polarization over these transition potentials will cause damage to the surface polymer layer, leading to an increased surface area of carbon fiber exposed and a sudden increase in polarization current density, which will be discussed below. The occurrence of these anodic and cathodic transitions at more anodic and cathodic potentials than those of the ground CFRPs could be due to the large IR drops in the pores of the surface polymer layers.

On E-CFRP, because of the thicker surface polymer layer and the less and non-uniformly distributed defects, the repeatability of EIS measurements is much worse than that on T-CFRP. For the same reasons, the resistance of the surface polymer layer of the former is a few orders of magnitude higher than that of the latter (Table II).

The different EIS behaviors (Figure 8) of the two CFRPs can also result from their different surface layer structures. The more
defects in the thinner surface polymer layer on T-CFRP than on E-CFRP mean that the resistance of the surface polymer layer $R$ is much higher on E-CFRP than on T-CFRP. It should be noted that a diffusion process ($Z_n$) in water can always be involved in both the E-CFRP and T-CFRP. However, due to the larger $R$ of the E-CFRP, the time-constant corresponding to $RC$ is considerably large. Thus, in the measured EIS of E-CFRP, $Z_n$ usually appearing at low frequencies may be overwhelmed by the $RC$ determined capacitive loop.

The $C$ values of the two CFRPs are very low in the order of magnitude of $10^{-5}$ F/cm$^2$, meaning that the $C$ is not a double layer capacitor (Table II). The CFRPs in solution act like a capacitor with the outmost carbon fiber bundle surfaces in the polymer matrix. The CFRP surfaces act as electric charging layers and the surface polymer layer as the dielectric. After surface grinding, the $C$ simply represents the double layer capacitance of the interface between the exposed carbon fibers and the test solution. Thus, the $C$ values of these two CFRPs reach the order of magnitude of $10^{-3}$ F/cm$^2$ (Table III), in the level of a double layer capacitor.

**Effective defects.**—In a CFRP, polymer matrix is inert and electrochemical reactions can only occur on the carbon fiber reinforcement, which means that only those carbon fiber surface exposed to the solution has a contribution to the electrochemical behavior of the CFRP. Thus, the micro-pores or defects that penetrate through the surface polymer layer determine the exposure of the electrochemically active carbon fiber under the surface polymer layer. They are effective defects, and the others not penetrating through the surface layer cannot affect the electrochemical performance of the CFRP.

To characterize the effective porosity, the electrochemical results of the CFRPs before and after surface grinding should be compared. The current densities of the E-CFRP ($I_E$) and T-CFRP ($I_T$) at the OCPs should be from the carbon fiber surface areas directly exposed to the test solution through the effective defects. They can be estimated to be $I_E = 5.5 \times 10^{-7}$ A/cm$^2$ and $I_T = 2.9 \times 10^{-7}$ A/cm$^2$ from the polarization curves (Figure 7) through Tafel extrapolation. These current densities at the OCPs after surface grinding become $3.6 \times 10^{-6}$ A/cm$^2$ and $5 \times 10^{-6}$ A/cm$^2$, respectively. Therefore, the effective porosity can be calculated from the ratio of the current density before surface grinding over that after surface grinding. They will be $1.53 \times 10^{-2}$ for E-CFRP and $5.8 \times 10^{-2}$ for T-CFRP. T-CFRP is more porous than E-CFRP. This strongly supports characteristic (3) of the proposed surface polymer model. The effective porosity calculation also indicates that most of the visible defects on the surfaces are actually ineffective pores.

The EIS measurements can also provide some information of the surface polymer layer. If the effective porosity of the surface polymer layer is simply assumed to be the ratio of the carbon fiber area exposed to the solution through the effective defects over the total exposed carbon fiber surface area after the surface polymer layer is removed, then the porosity is $4.11 \times 10^{-2}$ for E-CFRP and $2.96 \times 10^{-2}$ for T-CFRP can be obtained, which are about 2 orders of magnitude lower than those estimated by the current densities at the OCPs. This means that the carbon fiber surface exposed to the solution through the effective defects is not primary responsible for the capacitance $C$ of the surface polymer layer. The effective porosity is actually very small compared with the total porosity. In fact, due to the large number of defects distributed in the surface polymer layer, the capacitance of the polymer layer/carbon fiber interface can be influenced and overwhelmed by the distributed capacitance along sinus micro-pores to a great extent. Thus, the interface capacitance has a very limited contribution to the measured $C$ value. The capacitance obtained through EIS measurement should mainly result from the charging and discharging over the outer and inner surfaces of the surface polymer layer (the inner surface refers to the interface of the surface polymer layer and carbon fiber). Due to the large thickness of the surface layer, $C$ is considerably lower than a normal double layer capacitance. The dielectric of the polymer and all the defects (micro-pores), including the effective defects, can significantly influence the $C$ value. It is difficult to attribute the different $C$ values of the E-CFRP and T-CFRP to any individual factors. The E-CFRP has many micro-gaps, which have a contribution to the distributed capacitance value. Hence, its $C$ value is not very low compared with that of the T-CFRP, although its surface layer is much thicker than that of the T-CFRP.

**Surface damage by polarization.**—The breakdown of the surface layers of the CFRPs under strong anodic and cathodic polarization may result from pH change of the test solution or gas bubbles released from the carbon fiber underneath. As the oxygen generation and hydrogen evolution under strong anodic and cathodic polarization conditions can lead to acidification and alkalization locally at the electrode surface, the possible damage to CFRPs caused by the change in local pH value should be examined. The immersion experiments in the solutions with different pH values indicate that the change in solution pH cannot cause damage to the surface polymer layers in reality (Figure 14). Therefore, the pH change induced damage can be excluded in this study. Certainly, a relatively high local concentration of H$_2$O$_2$ could also cause oxidative damage to the composite.36,45 However, under normal polarization conditions without required catalysts, the main reactions are hydrogen evolution and oxygen generation. It is unlikely to generate a significant amount of such oxidant. Therefore, the possibility of H$_2$O$_2$ induced degradation can also be excluded in this study.

The growth of gas bubbles on the CFRP surfaces under anodic and cathodic polarization conditions must be a result of the anodic oxygen generation (4OH$^-$ = O$_2$+$2H_2O$+4e$^-$) and cathodic hydrogen evolution (2H$_2$O+2e$^-$ = H$_2$+2OH$^-$) on the carbon fiber surface exposed to the solution through effective defects (see Figure 13). It is a physical effect, which can be easily understood according to the surface polymer layer model (Figure 15). Most of the gaps are at the polymer/carbon fiber interface in the E-CFRP. If these gaps are in connection with effective defects, then the growth of the gas bubbles trapped there will definitely tear off the surface polymer layer from inside.

According to the model (Figure 15), there is no doubt that the breakdown of the surface layer can lead to a sudden increase in current density, i.e., a transition point, on the potentiodynamic polarization curves (see Figures 7). Under anodic polarization, when the voltage reaches 1.5V (vs OCPs), O$_2$ evolution starts on the carbon fiber surface areas under the effective defects. The generated O$_2$ tends to push the polymer layer away there, resulting in more carbon fiber surface area exposed to the solution in the expanded effective defect. A similar cathodic hydrogen evolution can occur on the carbon fiber surface areas under the effective defects when the polarization voltage reaches $-2V$ (vs OCPs), which would cause the same damage to the surface polymer layer as the anodic polarization. More positive anodic or more negative cathodic polarization would lead to more severe damage to the surface layers. Figures 7, 13 and 14 suggest that the breakdown of the surface layers of CFRPs under strong anodic and cathodic polarization conditions in the test solution can be predicted from their potentiodynamic polarization curves.

**Conclusions**

1. The bulk resistance values of the E-CFRP and T-CFRP are as low as a metal. The surface polymer layers do not have a contribution to their resistivity, because the carbon fiber bundles are responsible for their electrical conductivity. Therefore, the E-CFRP and T-CFRP have different bulk resistance values due to the different amounts and distributions of carbon fiber bundles in epoxy and nylon.

2. The surface polymer layer critically influences the electrochemical performance of a CFRP. The E-CFRP and T-CFRP have different EIS and polarization behaviors because of the different microstructures or defects in their surface polymer layers. The surface epoxy layer of E-CFRP is thicker, contains less effective defects and has more gaps at the interface between epoxy and the polymer/carbon fiber interface in the E-CFRP. When the voltage reaches 1.5V (vs OCPs), O$_2$ evolution starts on the carbon fiber surface areas under the effective defects. The generated O$_2$ tends to push the polymer layer away there, resulting in more carbon fiber surface area exposed to the solution in the expanded effective defect. A similar cathodic hydrogen evolution can occur on the carbon fiber surface areas under the effective defects when the polarization voltage reaches $-2V$ (vs OCPs), which would cause the same damage to the surface polymer layer as the anodic polarization. More positive anodic or more negative cathodic polarization would lead to more severe damage to the surface layers. Figures 7, 13 and 14 suggest that the breakdown of the surface layers of CFRPs under strong anodic and cathodic polarization conditions in the test solution can be predicted from their potentiodynamic polarization curves.
carbon fiber bundles than those of T-CFRP. Therefore, the former has low polarization current densities and higher impedance.

(3) Although E-CFRP and T-CFRP are very stable in neutral, acidic and alkaline environments at their OCPs in this study, their surface epoxy and nylon layers can break down under strong anodic and cathodic polarization conditions. The damage is caused by anodic oxygen generation and cathodic hydrogen evolution from the carbon fiber underneath the surface polymer layers. This implies that a E-CFRP or T-CFRP maybe electrochemically damaged if a stray current is following in or out it, which could occur in a cathodic protection system or a system with bad ground connection.

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