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## Advanced anticorrosive materials prepared from amine-capped aniline trimer-based electroactive polyimide-clay nanocomposite materials with synergistic effects of redox catalytic capability and gas barrier properties

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### ABSTRACT

In this study, preparation and electrochemical corrosion protection studies of a series of polyimide—Clay nanocomposite (PCN) materials were first presented. Subsequently, the as-prepared PCN materials were characterized by FTIR, XRD and TEM studies. *In-situ* monitoring for redox behavior of as-prepared PCN materials was identified by UV—visible and CV studies.

It should be noted that PCN coating was found to reveal advanced corrosion protection effect on coldrolled steel (CRS) electrode as compared to that of neat non-electroactive polyimide coating based on series of electrochemical corrosion measurements in 5 wt% NaCl electrolyte. Enhancement of corrosion protection of PCN coatings on CRS electrode may be interpreted by following two possible reasons: (1) redox catalytic capabilities (*i.e.*, electroactivity) of ACAT units existed in electroactive PCN may induce formation of passive metal oxide layers on CRS electrode, as evidenced by SEM and ESCA studies. (2) well-dispersed layered organophilic clay platelets embedded in electroactive PCN matrix could functioned as hinder with high aspect ratio to effectively enhance the oxygen barrier property of PCN, as evidenced by GPA.

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### 1. Introduction

In the past decades, electronically conducting polymers have been classified as a new class of soft materials and attracted extensive research activities because they exhibited reversible doping/dedoping properties and redox capability (*i.e.*, electroactivity), which may lead these polymers exhibiting broad spectrum of potential commercial applications in electronic, optical and biological research fields. Among those conducting polymers, polyaniline (PANI) evoked more attractions due to its environmental stability and relatively low cost [1,2]. However, the poor solubility of PANI in common organic solvents limits its applications in many fields. Therefore, several research groups have devoted their great efforts to improve the processability of PANI by various approaches [3–6].

Research activities have been focused particularly on the synthesis of aniline oligomers with well-defined structures and

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end-groups because of their good solubility and ability to undergo further polymerization. Synthesis of a number of aniline oligomers has been reported [7–12]. For example, Honzl and Tlustakova [10] prepared a series of phenyl-capped aniline oligomers with 2, 3, 4 and 6 amine units through complicated synthesis. In a landmark paper, published in 1986, Wudl et al. reported the synthesis of phenyl-capped octaaniline by reacting tetraaniline with dihydroxyterephthalic acid [11]. However, most synthetic routes involved multi-step reactions or the use of unstable agents. Subsequently, Wei et al. developed a convenient and one-step method to synthesize a series of aniline oligomers with welldefined structures and end-groups via chemical oxidation of aniline and its analogue compounds [13].

Recently, electroactive polymers resulted from aniline oligomers have attracted intensive research interests due to they exhibited similar reversible doping/de-doping and redox properties of parent PANI [14–21]. For instance, Zhang and Wei et al. reported that the synthesis and characterization of aniline pentamer-based electroactive polyamide and polyimide prepared from oxidative coupling polymerization [17–20]. Moreover, Yeh et al. reported the evaluation of corrosion protection of amine-capped

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aniline trimer-based electroactive polyimide and epoxy resin coating on metallic electrode based on a series of electrochemical corrosion measurements on saline conditions [22,23]. In this report, they found that the redox catalytic property of as-prepared electroactive polyimide or epoxy resin may induce the formation of densely passive oxide layer, as identified by the ESCA studies, to protect the underlying metal against the attacking of aggressive species, similar to the corrosion protection mechanism of PANI reported by other research groups [23,24].

On the other hand, clay-based polymeric nanocomposite materials attracted great research interests lately because of the clay platelets with high aspect ratio was found to boost the physical properties of neat polymers such as mechanical strength, thermal stability, fire retardant, gas barrier [25]. Moreover, clay-based polymeric nanocomposite coatings were also found to exhibit excellent anticorrosive performance on metallic substrate, which is associated with the well-dispersed clay platelets in various polymeric coatings leading to the effective increase the length of diffusion pathways for oxygen and water as well as decrease the permeability of the coating. Yeh et al. reported that the polymer–clay nanocomposite coatings revealed better anticorrosive performance as compared to that of corresponding neat polymeric coating by performing a series of electrochemical corrosion measurements in saline [25–29].

To the best of our knowledge, electroactive polyimide–clay nanocomposite (PCN) materials have not been reported. Therefore, in this study, we attempt to prepare an advanced PCN anticorrosive coating materials with synergistic effects of redox catalytic capability and gas barrier properties by incorporation of well-dispersed organophilic clay platelets into amine-capped aniline trimer (ACAT)-based electroactive polyimide matrix through chemical imidization. Corrosion protection of electroactive PCN coatings was investigated by a series of electrochemical measurements such as corrosion potential ( $E_{corr}$ ), polarization resistance ( $R_p$ ) and corrosion current ( $I_{corr}$ ) studied in 5 wt% NaCl electrolyte. Gas barrier properties and redox behavior (*i.e.*, electroactivity) of PCN materials, in the form of membrane and coating, was identified by the studies of gas permeability analysis (GPA) and electrochemical cyclic voltammetry (CV), respectively.

### 2. Experimental

### 2.1. Materials

Aniline (Sigma–Aldrich) was doubly distilled prior to use. 1,4phenylenediamine (Sigma–Aldrich), *N*,*N*-dimethylacetamide (DMAc; Mallinckrodt/Baker, Paris, KY), 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BSAA; Sigma–Aldrich, 97%), 4,4'-Oxydianiline (ODA; Fluka), (4-Carboxybutyl)triphenylphosphonium bromide (Sigma–Aldrich), were used as received without further purification. Montmorillonite clay (PK805), purchased from Pai-Kong ceramic company (Taiwan), was used, and had a CEC value of 98 meq/100 g. All reagents were reagent grade unless otherwise stated.

### 2.2. Instrumentations and measurements

Mass spectra were run on a Bruker Daltonics IT mass spectrometer model Esquire 2000 (Leipzig, German) with an Agilent ESI source (model G1607-6001). <sup>1</sup>H NMR spectra were run on a Bruker 300 spectrometer, referenced to internal standard of tetramethylsilane (TMS), DMSO was used as solvent. Fourier transform infrared spectroscopy (FTIR) spectra was obtained at a resolution of 4.0 cm<sup>-1</sup> with a FT/IR spectrometer (FT/IR-4100) at room temperature ranged from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. UV–visible absorption spectroscopy was obtained using a Hitachi U-2000 UV–visible spectrometer. Passivation metal oxide layers form on the CRS electrode were characterized by scanning electron microscopy (SEM) (Hitachi S-2300) and electron spectroscopy for chemical analysis (ESCA, VG Scientific ESCALAB 250). Observation of dispersion of clay was done using TEM images of nanocomposites were obtained with JEOL-200FX operated at an accelerating voltage of 120 kV. Electrochemical measurements of corrosion potential, polarization resistance, and corrosion current of coated cold-rolled steel (CRS) electrodes were obtained using VoltaLab 40 potentiostat/galvanostat with an electrochemical corrosion cell consisting of graphite rod counter electrode, SCE reference electrode and working electrode. Gas permeability (O<sub>2</sub> permeation) experiments were achieved using GTR-31 analyzer (Yangimoto Co., Kyoto, Japan).

### 2.3. Synthesis of amine-capped aniline trimer (ACAT)

A typical procedure was recently established by Wei et al. for the synthesis of ACAT and accordingly, ACAT could be easily synthesized by oxidative coupling of 1,4-phenylenediamine and 2 eq. aniline with ammonium persulfate as oxidant [13]. The detailed characterizations for the ACAT were listed as follows: MS: $[M - H]^+$  calculated, 289.1; found, 289.1. FTIR (KBr, cm<sup>-1</sup>): 3310 and 3209 (s,  $v_{NH}$ ), 1600 (s,  $v_{C=C}$  of quinoid rings), 1500 (vs,  $v_{C=C}$  of benzenoid rings), 1273 (s,  $v_{C-N}$ ), 823 (m, *para*-substitution of benzene ring) [16]. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO):  $\delta = 6.6-7.1$  (multiplet for 12H from aromatic ring),  $\delta = 5.5$  (2H, due to  $-NH_2$ ). The MS, FTIR and <sup>1</sup>H NMR spectrum of ACAT is shown in Fig. 1.

### 2.4. Preparation of organophilic-MMT clay [27]

Organophilic clay was prepared by a cationic—exchange reaction between sodium cations of MMT clay and quaternary phosphonium cations of intercalating agent. Equation for calculating intercalating agent used for cationic—exchange reaction was given as follows:

# $X = 98/100 \times 5 \text{ g (for clay)} \times 1.2 \times M_{\text{W}} \text{ (of intercalating agent)} \\ \times 1 \times 1/1000$

Where *X* represented the amount of used intercalating agent, 98/100 represent CEC value per 100 g of MMT clay, 1.2 (>1) indicating the excess amount of intercalating agent was used. Typically, 5 g of MMT clay, with a CEC value of 98 meq/100 g, was stirred in 400 mL of distilled water (breaker A) overnight at room temperature. A separate solution containing an excess amount of intercalating agent (2.6 g) in another 30 mL of distilled water (breaker B) was magnetically stirred, followed by the addition of 1.0 M HCl aqueous solution to adjust the pH value to about 3-4. After the solution was stirred for 1 h, the protonated amino acid solution (breaker B) was added at a rate of 10 mL/min, with vigorous stirring, to the MMT suspension (beaker A). Mixture was stirred overnight operated at room temperature. Organophilic clay was recovered by ultracentrifugating (9000 rpm, 30 min) and filtering the solution in a Buchner funnel. Washing and filtering of samples were repeated at least three times to remove any excess ammonium ions.

## 2.5. Synthesis of electroactive polyimide (EPI) and non-electroactive polyimide (NEPI)

Two types of polyimide were prepared for comparative studies: First of all, EPI was synthesized with ACAT and BSAA. On the other hand, NEPI was synthesized with ODA and BSAA. A typical procedure to prepare electroactive polyimide (EPI) was given as follows: BSAA (0.26 g, 0.5 mmol) was dissolved into 4.0 g of DMAc at room temperature (denoted cup A). A separate solution containing ACAT



Fig. 1. Spectral studies on ACAT (a) MASS (b) FTIR and (c)  $^1\mathrm{H}$  NMR spectra.

(0.145 g, 0.5 mmol) dissolved in another 4 g of DMAc under mechanical stirring was also prepared under continuous stirring for 30 min (denoted cup B). Subsequently, cup A was mixed with cup B followed by additional magnetic stirring for 24 h at room temperature. It was subsequently poured onto the supporting substrate to form electroactive EPAA, followed by chemical imidization under vacuum at 200 °C for 12 h [23,25]. The representative preparation procedure of EPI was depicted, as shown in Scheme 1.

### 2.6. Preparation of electroactive polyimide-clay (EPC) hybrid films

To prepare the clay-based electroactive polyimide hybrid film, a representative procedure was given as follows: first of all, 0.145 g of as-prepared ACAT fine powder was dissolved into 4 g of DMAc under magnetic stirring for 30 min. Moreover, suitable feeding amount of organophilic-MMT clay were completely blending into previous solution under continuous stirring for another 1 h at room temperature (denoted cup A). Subsequently, 0.26 g of BSAA fine powder was incorporated into cup A at room temperature, followed by stirring for additional 24 h. It was then poured onto the

supporting substrate to form EPAA, followed by chemical imidization under vacuum at 200 °C for 12 h [23,25] to give a series of EPC hybrid membranes. The typical synthesis procedure for EPC was depicted, as shown in Scheme 1.

## 2.7. Electrochemical cyclic voltammetric studies on the electroactivity of as-prepared EPI and EPC

To investigate electroactivity of various sample-coated electrodes, electrochemical cyclic voltammetric (CV) experiments were employed on VoltaLab 40 (PGZ 301) analytical voltammeter by using conventional three-electrode system. All CV measurements were performed at one double-wall jacketed cell, covered with a glass plate, through which water was circulated from a YEONG SHIH B-20 thermostat to maintain a constant operational temperature of  $25 \pm 0.5$  °C. The as-prepared polyimide film-coated electrode was prepared by casting as-prepared polymer solution in DMAc (0.25 M) on top of the working electrode and then drying it used of hotplate in air. Indium tin oxide (ITO) glass substrate was acted as working electrode, platinum wire and saturated calomel electrode (SCE)



Scheme 1. Schematic representation of the synthesis of ACAT and EPI/EPC.

were used as counter and reference electrode, respectively. Working electrode coated with polyimide thin film followed by cyclic potential between -0.2 and 1.0 V with scan rate of 50 mVs<sup>-1</sup> in 1.0 M H<sub>2</sub>SO<sub>4</sub>. Electrochemical CV measurements of all samples were repeated at least three times to ensure reproducible consistency.

### 2.8. Electrochemical corrosion evaluations of EPI and EPC

To measure the electrochemical corrosion performance of sample-coated CRS electrode, a series of EPAA were first cast dropwisely onto the CRS coupons (1.0  $\times$  1.0 cm), followed by chemical imidization in air at operational temperature of 200 °C for 12 h to allow evaporation of solvent molecules, giving an uniform and dense coatings of about 25  $\pm$  2  $\mu$ m in thickness, measured by digimatic micrometer (Mitutoyo, Japan). The coated and uncoated coupons were then mounted to working electrode so that only the coated side of the coupon was in direct contact with the electrolyte. Edges of electrodes were sealed with super fast epoxy cement (SPAR®). All electrochemical corrosion measurements were performed on a VoltaLab 21 (PGP 201) and repeated at least three times to ensure a reproducible result. All electrochemical corrosion measurements were performed at a double-wall jacketed cell, covered with a glass plate, through which water was circulated from a YEONG SHIH B-20 thermostat to maintain a constant operational temperature of 25  $\pm$  0.5 °C. As electrolyte, aqueous solutions of NaCl (5 wt%) were used. Open circuit potential (OCP) at the equilibrium state of the system was recorded as the corrosion potential ( $E_{corr}$  in mV versus SCE). Polarization resistance ( $R_p$  in  $\Omega$ / cm<sup>2</sup>) was measured by sweeping the applied potential from 20 mV below to 20 mV above the  $E_{\rm corr}$  at a scan rate of 10 mV/min and recording the corresponding current change.  $R_p$  value was obtained from the slope of the potential-current plot. The Tafel plots were obtained by scanning the potential from 250 mV below to 250 mV above the  $E_{\text{corr}}$  at a scan rate of 10 mV/min. Corrosion current ( $I_{\text{corr}}$ ) was determined through superimposing a straight line along the linear portion of the cathodic or anodic curve and extrapolating it through  $E_{\text{corr}}$ . Corrosion rate ( $R_{\text{corr}}$ , in millimer per year) was calculated from the following Equation (1):

$$R_{\rm corr}(\rm mm/year) = \frac{[I_{\rm corr}(A/cm^2) \bullet M(g)]}{D(g/cm^2) \bullet V} \times 3270$$
(1)

where *I* is the current (A/cm<sup>2</sup>), *M* is the molecular weight, *V* is valence, 3270 is constant and *D* is the density (g/cm<sup>3</sup>). All



**Fig. 2.** Wide-angle power X-ray diffraction patterns of (a) MMT (b) organophilic-MMT clay (c) EPC01 (d) EPC03 nanocomposite material.

experiments were operated at room temperature. All raw data were repeated at least three times to ensure reproducibility and statistical significance.

### 2.9. Gas barrier properties measurements

Gas permeability of membrane is determined by using the Yanaco GTR-31 gas permeability analyzer. Gas permeability is calculated by the following Equation (2):

$$P = l/(P_1 - P_2) \times \frac{q/t}{A}$$
<sup>(2)</sup>

where *P* is the gas permeability  $[cm^3 (STP) cm/cm^2 s cm Hg]$ , *q/t* is the volumetric flow rate of gas permeate  $[cm^3 (STP)/s]$ , *l* is the membrane thickness [cm], *A* is the effective membrane area  $[cm^2]$ , and *P*<sub>1</sub>, *P*<sub>2</sub> are the pressures (cm Hg) on the high-pressure and low-pressure sides of the membrane, respectively. The rate of transmission of O<sub>2</sub> is obtained by gas chromatography, from which the O<sub>2</sub> permeability is calculated [25,27].

### 3. Results and discussion

Oligomeric aromatic amines with amino groups at both ends attracted research interests in polymer science and industries because of their applications as model compounds for electroactive polyanilines and as monomers to prepare polyamides, polyimides and epoxy polymers [23,30]. Accordingly, trimer could be easily obtained in large quantity by oxidative coupling of *p*-phenylenediamine and aniline.



Fig. 3. TEM micrographs of (a) EPC01  $\times$  20 K (b) EPC03  $\times$  20 K.



Fig. 4. (a) UV-visible spectra monitoring chemical oxidation of EPAA. (b) A schematic presentation of the oxidation state change of amine-capped aniline trimer in EPAA.

### 3.1. Synthesis and characterization of organophilic-MMT clay

XRD is generally employed to characterize the interlayer spacing in clay particles, which is correlated with their extent of intercalation. The basal space indicates the interlayer spacing of silicate and is calculated from the peak position using the Bragg's formula  $n\lambda = 2d \sin \theta$ . Interlayer spacing of MMT clay ( $2\theta = \sim 6.8^{\circ}$ , d = 6.5 nm) increased after surface treatment with intercalating agent to 9.6 nm ( $2\theta = \sim 4.6^{\circ}$ ), as shown in Fig. 2. This result confirms that expansion of silicate layers in organophilic-MMT clay. At the same time, there are no obvious diffraction peaks for EPC01 and EPC03 nanocomposite in  $2\theta$  = 2–10° as opposed to the diffraction peak appeared at  $2\theta = 4.6^{\circ}$  (d-spacing = 9.6 nm) for organophilic-MMT clay, indicating the possibility of having exfoliated and intercalated silicate nanolayers of organophilic clay dispersed in the EPI matrix. In Fig. 3, TEM micrograph of EPI-clay materials, (a) 1 wt% and (b) 3 wt% loading, also show that the nanocomposite have a combinational morphology, including both exfoliated and intercalated nanolayered structures simultaneously in the polymer matrix.

### 3.2. Chemical oxidation of amine-capped aniline trimer (ACAT)based electroactive poly(amic acid) (EPAA) in the oxidation state of lecoemeraldine base

To elucidate the chemical oxidation of amine-capped aniline trimer (ACAT)-based electroactive poly(amic acid) (EPAA), the representative experimental step was given as follows: first of all, leucoemeraldine base (LB) of EPAA dissolved in DMAc obtained from previous preparative procedure was used as target solution. Chemical oxidation of target EPAA solution was *in-situ* monitored by UV–visible spectroscopy by introducing trace amount oxidant,  $(NH_4)_2S_2O_8$ , into target solution. For visible observation, the color transition of target solution was found to convert gradually from initial dark blue to final purple upon being oxidized, as shown in Fig. 4(a). In this study, EPAA in the oxidation state of



Fig. 5. Cyclic voltammetry of polyimide shown as (a) ITO (b) NEPI (c) EPI (d) EPC03 above were measured in aqueous  $\rm H_2SO_4$  (1.0 M) with scan rate of 50 mV/s.

Table 1	
Feed composition ratio and electrochemical corrosion measurements of the prepared materials.	

Sample code	Feed composition (g)			Electrochemical corrosion measurements						
	ODA	ACAT	BSAA	Organophilic clay	$E_{\rm corr}({ m mV})$	$R_{\rm p}  ({\rm k}\Omega  {\rm cm}^2)$	$I_{\rm corr}  (\mu A/cm)^2$	R <sub>corr</sub> (mm/year)	Thickness (µm)	P <sub>EF</sub> (%)
Bare <sup>a</sup>	-	_	_	-	-1020.9	2.47	9.14	$1.07 \times 10^{-1}$	-	-
NEPI	0.1	_	0.26	-	-900.2	5.09	4.02	$4.71 \times 10^{-2}$	25	1.06
EPI	_	0.145	0.26	-	-807.7	17.30	2.53	$2.96 \times 10^{-2}$	25	6.00
EPC01	_	0.145	0.26	0.004	-664.9	36.67	1.89	$2.21 \times 10^{-2}$	24	13.85
EPC03	-	0.145	0.26	0.012	-528.5	69.99	1.09	$1.28 \times 10^{-2}$	27	27.34

<sup>a</sup> Pristine CRS used for test.

leucoemeraldine was found to exhibit only one characteristic absorption band (denoted band b, found at lower wavelength) at the position of 330 nm, which is associated with a  $\pi - \pi^*$  transition of conjugated ring system. During slowly oxidation period, this characteristic absorption band of EPAA appeared at the position of 330 nm was found to reveal an obvious transition of blue-shift, accompanied with the intensity decreasing. On the other hand, a new characteristic absorption band (denoted band a, found at longer wavelength) found at the position of 560 nm, which is assigned to the benzenoid to quiniod excitonic transition, was found to continually increased in intensity [31-34]. Possible reason (Fig. 4(b)) for this chemical oxidation phenomena of EPAA by incorporating oxidant may be explained as follows: During the continuous oxidation period of the ACAT-based EPAA in oxidation state of leucoemeraldine containing benzene rings, it reached the oxidation state of emeraldine, which showed a  $\lambda_{max}$  (band *b*) at lower wavelength of 330 nm. Subsequently, it was further oxidized to oxidation state of emeraldine containing quinoid rings, which exhibited a  $\lambda_{max}$  (band *a*) at longer wavelength of 560 nm.

This appearance of novel wavelength peak found at the position of 560 nm and wavelength peal transition varied from original wavelength of 330 nm to final wavelength of 310 nm (*i.e.*, blue-shift), indicated that EPAA have been oxidized from initial oxidation state of leucoemeraldine to final oxidation state of emeraldine upon incorporation of oxidant [31–34].

Moreover, this redox behavior of EPI and EPC can also be further identified by electrochemical cyclic voltammetry (CV) approach, as shown in Fig. 5. A representative procedure for the preparation of electrode and *in-situ* monitoring of CV curves can be given as follows: first of all, DMAc solution containing ~5 wt% of asprepared EPAA was cast onto working electrode of indium tin oxide (ITO) glass substrate, followed by evaporating used of hotplate to give thin solid films with ~30  $\mu$ m in thickness. Subsequently,



Fig. 6. Tafel plots for (a) Bare (b) NEPI (c) EPI (d) EPC01 (e) EPC03 measured in 5 wt% aqueous NaCl solution.

electrochemical CV behavior of EPAA-coated ITO electrode immersed in 1.0 M  $H_2SO_4$  was performed at scan range of -200-1000 mV and scan rate of 50 mV/s, respectively, as shown in Fig. 5. It should be noted that second cycle of obtained CV curves was used for further studies.

For example, electrochemical CV studies of indicated that EPC03, in the form of coating, showed single oxidation peak, which was closely similar to that of neat EPI [35]. For instance, the EPC03 revealed oxidation current ( $I_{ox}$ ) of 169.60  $\mu$ A/cm<sup>2</sup> and reduction current ( $I_{red}$ ) of 336.31  $\mu$ A/cm<sup>2</sup>, respectively, which was found to be slightly smaller than that of EPI ( $I_{ox} = 169.31 \,\mu\text{A/cm}^2$ ,  $I_{red} = 347.35 \,\mu\text{A}/cm^2$ cm<sup>2</sup>). However, CV curve of NEPI was found to exhibit zero redox current, indicated that feeding conjugated diamine of ACAT may also incorporating electroactivity into as-prepared PI. Moreover, welldispersing of clay platelets into EPI matrix exhibited almost without sacrificing electroactivity. We therefore envisioned that the EPC, in the form of coating, may reveal advanced corrosion protection performance resulted from the synergistic effect of redox catalytic property of organic electroactive polyimide coating and gas barrier properties of well-dispersed inorganic organophilic clay platelets based on electrochemical cyclic voltammetry and gas permeability analysis, as discussed in the following sections.

### 3.3. Potentiodynamic measurements

In this section, corrosion protection of sample-coated CRS coupons can be observed from values of corrosion potential ( $E_{corr}$ ),



**Scheme 2.** Schematic diagrams of (a) mechanism of CRS passivation by EPC coatings. (b) diffusion pathway of oxygen gas in the EPC.



Fig. 7. SEM surface image of (a) polished CRS and (b) CRS induced by EPC03.

polarization resistance ( $R_p$ ), corrosion current ( $I_{corr}$ ), and corrosion rate ( $R_{corr}$ ), as listed in Table 1.

Polarization resistances,  $R_p$ , were evaluated from Tafel plots, according to Stearn–Geary Equation (3) [36–38],

$$R_{\rm p} = \frac{b_{\rm a}b_{\rm c}}{2.303(b_{\rm a} + b_{\rm c})I_{\rm corr}}$$
(3)

Here,  $I_{corr}$  is corrosion current determined by an intersection of linear portions of anodic and cathodic curves,  $b_a$  and  $b_c$  are anodic and cathodic Tafel slopes ( $\Delta E/\Delta \log I$ ), respectively.

Protection efficiency ( $P_{EF}$ %) values were estimated using following Equation (4) [39]:

$$P_{\rm EF}\% = \frac{R_{\rm P}^{-1}(\text{uncoated}) - R_{\rm P}^{-1}(\text{coated})}{R_{\rm P}^{-1}(\text{coated})} \times 100\%$$
(4)

CRS coupon coated with EPI shows a higher  $E_{corr}$  value than NEPI-coated CRS, which is consistent with previous observations [23]. However, it exhibited a lower  $E_{\rm corr}$  value than the specimen coated with EPC materials. For instance, EPC03-coated CRS has a high corrosion potential of ca. -528 mV at 30 min. Such  $E_{corr}$  value implied that EPC03-coated CRS more noble towards electrochemical corrosion compared to EPI. The EPC03-coated showed a polarization resistance ( $R_p$ ) value of 69.99 K $\Omega$  cm<sup>2</sup> in 5 wt% NaCl, which is about one order of magnitude greater than the uncoated CRS. The Tafel plots for (a) uncoated, (b) NEPI-coated, (c) EPIcoated, (d) EPC01-coated, and (e) EPC03-coated CRS are shown in Fig. 6. The corrosion current  $(I_{corr})$  of EPC03-coated CRS is *ca*. 1.09  $\mu$ A/cm<sup>2</sup>, which was correspondent to a corrosion rate ( $R_{corr}$ ) of ca. 1.28  $\times$  10<sup>-2</sup> mm/year (Table 1). Electrochemical corrosion current and corrosion potential of EPC materials as coatings on CRS were found to decrease gradually with further increase in Clay loading. Mechanism of enhanced corrosion protection of EPC coatings was found to be associated with the formation of passivation protective metal oxide layers, inducing from the redox catalytic properties of ACATs units existed in as-prepared EPC coatings, as shown in Scheme 2(a), which was similar to that of PANI coatings reported in the previous literatures [40–42]. Enhanced corrosion protection effect of EPC coatings compared to neat EPI might be resulted from well-dispersing organophilic clay platelets in EPI matrix to increase the tortuosity of diffusion pathway of oxygen gas. This can be further evidenced by studies of O2 gas permeability in EPC membranes as discussed in following section.

### 3.4. Observations and investigation on CRS surface

In the present work, the as-prepared sample coatings were then removed by razor knife. Visual observation of passivation oxide layers exhibited the deposition of grayish oxide layer form over the CRS surface [43,44] under EPC coating on CRS electrode. SEM image studies revealed that oxide layers were formed at the interface of EPC (i.e., EPC03) coating and CRS surface (Fig. 7(b)). However, we could not observe same image of passive metal oxide layer from bare CRS surface (Fig. 7(a)). In addition to the SEM observations, chemical nature of passivation oxide layers can also be identified by the investigation of ESCA. Typical procedure for sample preparation of ESCA was listed as follows: Surface of CRS electrode were first coated with EPI coating with  $\sim$  45  $\mu$ m in thickness, followed by exposing/ immersing into 5-wt% of aqueous NaCl electrolyte for period time of 24 h. Subsequently, the EPI layer was removed and the passive metal oxide layer induced from the redox catalytic property of EPI was further examined by ESCA studies. It should be noted that Fe  $2_{p3/2}$ peak binding energy of Fe<sub>2</sub>O<sub>3</sub>, FeO and Fe<sub>3</sub>O<sub>4</sub> was found to appear at the position of 710.9, 709.6 and 710.3 eV, respectively. The typical binding energy plots versus intensity for iron oxide layers were shown in Fig. 8. Fe 2p spectra of FeO and Fe<sub>3</sub>O<sub>4</sub> are very similar and it is hard to distinguish from each other. Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$  binding energy were found at the position of about 724.2 and 711.0 eV. It was indicated that the passive oxide layer is predominately composed by Fe<sub>2</sub>O<sub>3</sub>, above a very thin Fe<sub>3</sub>O<sub>4</sub> layer [24].

### 3.5. Gas barrier properties

Presence of inorganic or organic fillers in polymer matrix usually constitutes solid barrier in the path of gas molecules passing through polymer. A more tortuous path is thus forced upon



Fig. 8. ESCA Fe 2p core level spectra of EPI.



Fig. 9. Permeability of O<sub>2</sub> as a function of clay content in EPC nanocomposite materials.

gas molecules passing through polymeric matrix, retarding the progress of the phenomenon. The more tortuous the path the longer it takes for the gas molecules to pass through the material. resulting in a macroscopically observed reduced permeability. The higher interfacial area of filler-matrix and aspect ratio of filler, the more tortuous path, hence the greater decrease in permeability. Clay-based polymer nanocomposites had been examined intensively for their gas barrier rate's enhancements, due to the high aspect ratio of well-dispersed organophilic clay platelets [45]. In this study, oxygen gas (molecular) permeability analysis of EPI and EPC membranes was investigated with  $\sim$ 45 µm in film thickness. Compared to NEPI and EPI, the EPC membranes were found to exhibit lower O<sub>2</sub> permeability, as shown in Fig. 9. For example, O<sub>2</sub> permeability of EPC01 and EPC03 were found to be 0.34 and 0.31 barrer, respectively, which was obviously lower than that of 0.68 barrer for NEPI and 0.44 barrer for EPI. Moreover, it should be noted that O<sub>2</sub> permeability of NEPI is higher than EPI, indicating that EPI membrane exhibiting dense packed structure formed by the intra-molecular interactions such as  $\pi - \pi$  stacking between aromatic rings of ACAT segments [46]. Furthermore, compared to EPI, EPC membranes at 3 wt% clay loading was found to show  $\sim 30\%$ reduction in O<sub>2</sub> permeability. This result could be associated with better dispersion of clay platelets in EPI matrix (as identified in TEM micrograph), which may lead to a remarkably increased tortuosity of the diffusion pathway of oxygen, as shown in Scheme 2(b). It should be noticed that a further increase loading of clay platelets in polymer matrix may result in a further enhanced molecular barrier property in as-prepared EPC membranes.

### 4. Conclusion

In this study, we present the first preparation and corrosion protection studies of a series of electroactive polyimide-clay (EPC) nanocomposite materials containing conjugated segments of electroactive amine-capped aniline trimer (ACAT) and welldispersed organophilic clay platelets. First of all, the amine-capped aniline trimer (ACAT) was synthesized by oxidative coupling reactions between 1,4-phenylenediamine and aniline with ammonium persulfate as oxidant, followed by characterized by mass spectroscopy (MS), Fourier-transformation infrared (FTIR) and <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy. Subsequently, the EPC materials were prepared by performing the chemical imidization of EPI in the presence of organophilic clay platelets. Dispersion capability of organophilic clay in EPI matrix was further identified by wide-angle powder X-ray diffraction (XRD) pattern and transmission electron microscopy (TEM). In-situ monitoring of chemical oxidation of EPI solution by gradually incorporation of oxidant was investigated by UV-visible absorption spectroscopy. Electroactivity and gas permeability of as-prepared EPC, in the form of coatings and membranes, was identified by electrochemical cyclic voltammetry (CV) and gas permeability analysis (GPA) studies, respectively. It should be noted that EPC containing different loading of well-dispersed organophilic clay platelets still exhibited reversible redox current very similar to that of neat EPI, as evidenced by CV studies.

The as-prepared EPC coatings were found to exhibit advanced corrosion protection efficiency as compared to that of NEPI, EPI and bare CRS electrodes based on the sequential electrochemical corrosion measurements in saline condition. The significant enhancement in corrosion protection of EPC coatings on CRS electrodes might probably be attributed to the redox catalytic property of organic EPI inducing the formation of passive metal oxide layer and the barrier property of well-dispersed organophilic clay platelets existed in EPI matrix, as evidenced by the investigated by the SEM/ESCA and GPA studies, respectively.

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