



Functionalised graphene as a barrier against corrosion



Karanveer S. Aneja^a, H.L. Mallika Böhm^c, A.S. Khanna^a, Siva Böhm^{a,b,*}

^a Department of Metallurgical Engineering and Materials Science, IIT Bombay, Powai, Mumbai, India

^b Talga Advance Materials GmbH, Prof.-Hermann-Klare-Str. 25, 07407 Rudolstadt, Germany

^c Warwick Technology Center, Voyager Building, University of Warwick Science Park, Sir William Lyons Road, Coventry CV4 9XF, UK

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ABSTRACT

The present work investigates the barrier protection mechanism of functionalised graphene when coated on mild steel substrate. Electrochemical parameters of the coating such as pore resistance, coating capacitance and water uptake characteristics were evaluated using electrochemical impedance spectroscopy. Additionally, breakpoint frequencies were deduced to evaluate the electrochemical activity at the surface over time. These electrochemical results in combination with the structural analysis of the coating help in developing a systematic understanding of the barrier properties rendered by graphene.

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1. Introduction

The use of graphene against corrosion has been widely reported in the past [1–9] but studies involving mechanistic understanding are limited. Böhm [1] describes the plausible reasons for anti-corrosive applications of graphene are its high surface area, its ability to provide a barrier against corrosive species and its excellent electrical conductivity. A systematic understanding of each of these parameters will lead to a better understanding of the corrosion protection mechanism of graphene.

A corrosion (anodic) reaction occurs in an electrolytic medium along with a cathodic reaction which balances the net charge. Water molecules that permeate through the coating provide an electrolytic medium for the corrosion reaction to take place. Further, it can induce internal stresses in the coating and cause physical swelling [10].

Water uptake can be calculated by either measuring the weight change on exposure to atmosphere (gravimetric technique) or by measuring the changes in coating's electrical capacitance (capacitive technique) over long exposure to aqueous environments using electrochemical impedance spectroscopy (EIS). Gravimetric technique can incorporate experimental errors when thin coatings are to be investigated [11]. Capacitive technique

provides a better estimate for thin coating systems and is based on the principle that water permeation increases the capacitance of the coating [10]. Further, by using capacitance measurements, coating properties such as diffusivity and equilibrium water content can also be obtained [12]. Other possible techniques include differential scanning calorimetry (DSC) [13], which only detects water in clustered form and FTIR [14], which can only provide a qualitative assessment.

The onset and propagation of coating damage are important parameters in determining the effectiveness of a particular coating system. Experimentally, it is quite difficult to deduce these parameters. Breakpoint frequency method is a simple yet powerful technique to determine the onset and propagation of coating degradation using empirically derived equations without the need to physically measure the coating damage [15]. Studies proposed by Hirayama and Haruyama [16] and Scully et al. [17–19] allow determination of damaged area as small as 0.01%. This technique has been widely used in the past [15–23] to evaluate the effect of coating constituents on the performance of coating systems.

The present study combines water uptake and breakpoint frequency techniques to evaluate the effect of graphene as a barrier against corrosion. Although other plate like materials such as, exfoliated clays, glass flakes and micaceous iron oxide (MIO) have been traditionally used as pigments that render similar barrier properties to the primer coating, the advantage of using graphene and other 2D materials lie in their higher specific surface area, owing

* Corresponding author at: Department of Metallurgical Engineering and Materials Science, IIT Bombay, Powai, Mumbai, India.

E-mail address: siva@talgagmbh.com (S. Böhm).

to their two dimensional planar structure, which provides better coverage for the same amount of material used [1,2].

2. Experimental

2.1. Materials and coating

Electrochemically extracted graphene nano platelets (Talga Resources Limited – Vittangi Graphite Deposit) were used as raw material in this study [24]. High quality few layer graphene (1–3 layers) was prepared by high shear liquid exfoliation (8000 rpm for 6 h) in a solution containing deionised water (Millipore) and surfactants (Fig. 1). Characterisation of produced graphene has been discussed in an earlier work [2] of the authors.

3-(Aminopropyl)triethoxysilane (APTES), purchased from Alfa Aesar®, was hydrolysed with acidified demineralised water (pH = 5), and used to chemically modify (functionalise) different concentrations of graphene. The exact formulations are provided in Table 1.

The functionalised graphene formulations were applied on ultrasonically cleaned mild steel panels using a bar applicator (20 micron wet film thickness) (Fig. 2). Hydrolysed APTES (0% graphene) was used as a benchmark. Curing of these coatings was performed at 120 °C for 90 s however as explained in an earlier work [2], in order to evaporate unwanted additives, these coatings were further heat treated at a temperature of 200 °C in a vacuum oven.

2.2. Electrochemical Impedance measurements

Acrylic tubes were fixed onto the coated panels so that a panel area of 3.14 cm² could be exposed to the test solution i.e. 3.5 wt.% NaCl solution (freely exposed to air, pH 5.5 at 25 °C), for long durations. A standard three-electrode configuration was used with the substrate acting as a working electrode, saturated calomel electrode as a reference, and platinum mesh as the counter electrode. The impedance measurements were performed using Biologic SP300 potentiostat driven by EC-Lab software. The open circuit potential was considered to be stable when its fluctuation was less than 5 mV for a period of 1000 s.

2.3. Scanning electron microscopy

Coating cross sections of hydrolysed APTES and functionalised graphene coated mild steel were analysed using environmental scanning electron microscopy (FEI, Quanta 200 D 7548) for elemental mapping.

3. Results and analysis

Electrochemical impedance spectroscopy was carried out periodically; by applying a sinusoidal voltage of amplitude 10 mV at the corrosion potential (E_{corr}) and responses were measured over frequencies 10 mHz and 100 kHz, until the impedance values

matched with those of bare mild steel, indicating complete delamination of the coating.

Time dependent Bode and Nyquist impedance plots are shown in Fig. 3. For the sake of simplicity, time dependent plots of only functionalised graphene (5% graphene) are shown. The impedance values gradually decrease with increasing exposure times till about 480 h beyond which the impedance values match those of bare mild steel indicating complete delamination of the coating.

A comparison between functionalised graphene (5% graphene) and hydrolysed APTES (0% graphene) at the beginning of exposure ($t = 0$ h) is shown in Fig. 4. These plots clearly depict an order of magnitude difference in impedance values at the onset of exposure.

The data obtained were simulated using an analogue electrical circuit, shown in Fig. 5(a), to obtain coating parameters (plotted in Fig. 6) at regular intervals. The difference between modelled and experimental data was less than 5%. The modelled and experimental data are plotted in the form of Nyquist plot in Fig. 5(b).

Pore resistance (R_p) for all the formulations is initially high corresponding to intact barrier coating resistance but as water permeates, R_p approaches a saturated value. This effect can be explained by considering the growth of pathways through the coating as water permeates. Increase in R_p with increasing graphene concentration at any given time, as seen in Fig. 6(a), suggests a strong interlinked structure, arising due to the functionalisation of graphene, that resists migration paths for corrosive species.

The values of constant phase element (CPE) are converted to effective capacitance (C_{eff}), using Eq. (1) [25], in order to determine the water absorption parameters.

$$C_{\text{eff}} = Q^{1/n} R_p^{(1-n)/n} \quad (1)$$

n is the CPE parameter and is equal to 1 for pure capacitance.

Rapid increase in C_{eff} values followed by a plateau corresponding to saturation level is observed, as shown in Fig. 6(b). C_{eff} depends on the dielectric constant of the coating and hence on the water absorbed [11].

Since water absorption in coatings is assumed to be mainly due to diffusion [12], it is possible to obtain the diffusion coefficient using a particular solution of Fick's second law [26]

$$\frac{M_t}{M_s} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 D \pi^2 t}{L^2}\right) \quad (2)$$

M_t is the amount of water absorbed at any time t (s), M_s the maximum amount of water absorbed, L the coating thickness (cm) and D is the diffusion coefficient (cm² s⁻¹).

When considering short periods of time, Eq. (2) can be simplified to:

$$\frac{M_t}{M_s} = \frac{4\sqrt{D}}{L\sqrt{\pi}} \sqrt{t} \quad (3)$$

The capacitance method of evaluating water transport into coatings is based on the assumptions that the change in capacitance is entirely due to the permeation of water into the film, film swelling is negligible, and permittivity of absorbed water is constant [11]. Dependence of coating capacitance on water permeation can be understood by considering a simple capacitor whose capacitance is directly proportional to the relative dielectric constant ϵ of the coating and to the area A of the capacitor, and inversely proportional to the coating thickness d :

$$C = \frac{\epsilon \epsilon_0 A}{d} \quad (4)$$

ϵ_0 is the dielectric constant of free space (8.854×10^{-14} F/cm). Since the dielectric constant of water is high (78.3 at 25 °C) as

Table 1
Coating formulations.

Formulation	APTES (% by weight)	Water (% by weight)	Hydrolysed APTES (% by weight)	Graphene (% by weight)
1	39.96	59.94	99.9	0.1
2	39.8	59.7	99.5	0.5
3	39.6	59.4	99	1
4	38	57	95	5

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