



## Evaluation of multi-layered graphene nano-platelet composite coatings for corrosion control part II – Cathodic delamination kinetics



C.F. Glover<sup>b</sup>, C.A.J. Richards<sup>a,\*</sup>, G. Williams<sup>a</sup>, H.N. McMurray<sup>a</sup>

<sup>a</sup> Materials Research Centre, College of Engineering, Swansea University, Bay Campus, Fabian Way, SA1 8EN, Swansea, UK

<sup>b</sup> Centre of Electrochemical Science and Engineering, University of Virginia, McCormick Avenue, VA22904, Charlottesville, VA, USA

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### ABSTRACT

In-situ Scanning Kelvin probe (SKP) measurements are used to follow the corrosion-driven cathodic delamination kinetics of model coatings comprising graphene nano-platelets (GNP) dispersed in polyvinylbutyral (PVB) adherent to iron and zinc (galvanised steel). To reduce delamination rates by > 90% (relative to unpigmented PVB) a GNP volume fraction of 0.056 is required on iron but only 0.028 on zinc. On this basis, together with work function and O<sub>2</sub> permeability data it is proposed that the GNP acts principally to slow through-coating oxygen transport on iron; whereas on zinc a galvanic couple forms between zinc and GNP, displacing cathodic oxygen reduction.

### 1. Introduction

The benefit of graphene and graphene-composites for corrosion protection is a current topic of interest [1–5] and the principal mechanism by which inhibition occurs is a contentious issue. Many publications speculate that reduced permeation to oxygen and water is the principal mechanism, (Fig. 1b) [4,6–15]. Others suggest that the electrical conductivity of graphene enables it to support electron transfer reactions, displacing electrochemical activity away from the metal surface and into the graphene coating (Fig. 1c) [2,5,16]. These mechanisms are illustrated schematically in Fig. 1. Thus, in Fig. 1a an unpigmented, electronically non-conductive coating allows relatively facile O<sub>2</sub> transport and cathodic O<sub>2</sub> reduction occurs at the metal-coating interface. In Fig. 1b a GNP-polymer composite coating exhibits reduced O<sub>2</sub> permeability due to the increased tortuosity of O<sub>2</sub> diffusion pathways. In Fig. 1c electronic conduction pathways from the metal substrate through and interconnected network of GNP particles allows cathodic O<sub>2</sub> reduction to become displaced from the metal coating interface and into the coating. Conversely, it should be noted that making the coating a cathode might have a corrosion accelerating effect where metal is exposed at a coating defect due to coating-defect coupling. Here, we aim to establish the dominant mechanism for hot dip galvanised steel (HDG) and iron substrates using the Scanning Kelvin probe technique (SKP), and findings from Part I of this paper, to assess the effect of in-coating GNP on an important failure mechanism, cathodic delamination.

In the case of unpigmented polymer coatings, delamination is

driven by an electrochemical cell via the galvanic coupling of anodic metal dissolution in the defect region with cathodic oxygen reduction at the advancing delamination front (Eqs. (1) and (2) respectively) as depicted in the schematic in Fig. 2. The electrochemical reduction of molecular O<sub>2</sub> leads to the generation of OH<sup>-</sup> ions that render the cathodic delamination zone highly alkaline (i.e. > pH 10) [17,18].

The formation of hydroxyl radicals as intermediates in the cathodic reduction of oxygen has also been implicated in attacking the organic binder by oxidative degradation [17]. A thin, gel-like layer of electrolyte ingresses underneath the coating and loss of adhesion is widely attributed to alkaline attack on the coating-metal bond [19] (Eq. (2)).



In the current study, experiments were carried out on iron and HDG substrates in high humidity (95%) air where a 0.86 M aqueous NaCl electrolyte was added to a penetrating defect. By systematically varying the non-functionalised graphene nano-platelet (GNP) content dispersed in polyvinyl butyral (PVB) primer coatings in contact with the substrate, it was possible to assess the rate and time dependent order of cathodic delamination kinetics. The SKP technique is a well-established method for determining the kinetics of corrosion-driven organic coating failure/delamination, as a means of establishing the relative efficiency and inhibitive mechanisms of coating containing dispersed inhibitive pigments [20–24] and for various other corrosion studies [25–27]. The oxygen permeation, conductivity and Volta potential data presented in

\* Corresponding author.

E-mail address: [557333@swansea.ac.uk](mailto:557333@swansea.ac.uk) (C.A.J. Richards).

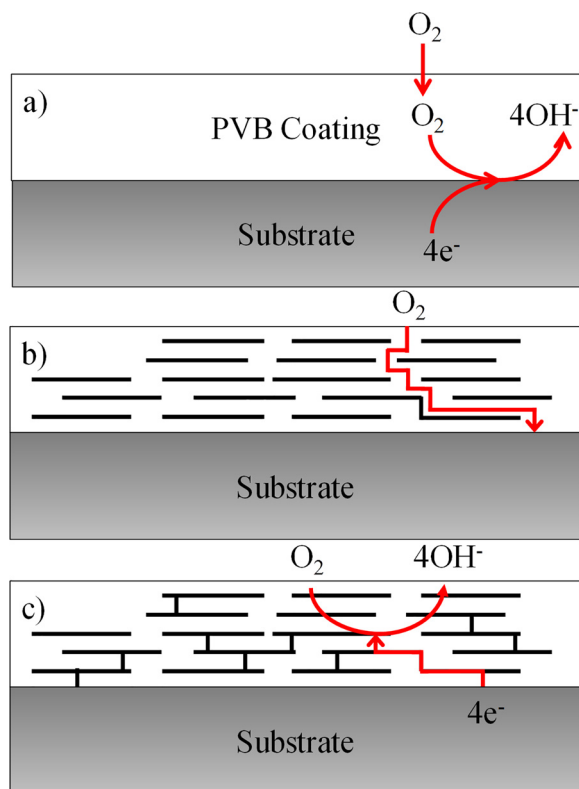


Fig. 1. Schematic showing three scenarios of cathodic delamination where: a) For uninhibited coatings, cathodic  $O_2$  reduction occurs at the coating/substrate interface b) in-coating GNP pigment may increase the tortuosity of  $O_2$  diffusion pathway c) in-coating GNP pigments may displace  $O_2$  reduction away from coating/substrate interface.

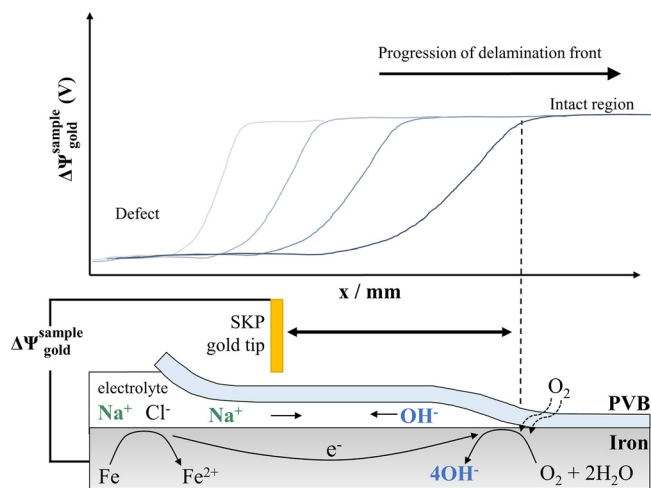


Fig. 2. Schematic representation of the corrosion-driven delamination cell showing correspondence with various regions of the time-dependent  $\Delta\Psi$  profile.

Part I of this paper have been used to support our hypotheses.

## 2. Materials and methods

### 2.1. Materials

Iron foil (99.99% purity) of 1.5 mm thickness was obtained from Goodfellow Metals Ltd. This was cut into square coupons of 50 mm  $\times$  50 mm. Hot dip galvanized steel (HDG) samples, provided by Tata Steel UK, comprising 0.7 mm gauge mild steel coated with a Zn layer of 20  $\mu\text{m}$  (also containing 0.2% Al) were also cut into square

coupons of 50 mm  $\times$  50 mm. All chemicals were supplied by Sigma-Aldrich Chemical Co and were of analytical grade purity. GNP pigment obtained from Haydale Ltd and characterized previously [34] was dispersed in PVB at various pigment volume fractions ( $\phi$ ) [34].

### 2.2. Methods

Design and operation of the SKP apparatus has been described extensively elsewhere [20,29,30]. The sample preparation procedure was based on the methods presented in work carried out by Stratmann et al. [19,29,33]. Polyvinyl butyral (PVB) solutions MW 70,000–100,000 were prepared in ethanol (15.5% w/w) and the required amount of GNP were added and thoroughly mixed. An aqueous slurry of 5  $\mu\text{m}$  alumina was used to hand-polish the sample surface to remove any contaminants and a pre-existing oxide layer. Degreasing was carried out via an acetone rinse followed by air-drying. PVB solution containing the appropriate amount of GNP was bar-cast onto a pre-cleaned sample and room-air dried. Strong film adhesion was observed in both wet and dry form where it was not possible for the film to be peeled off by hand.

All delamination experiments were carried out in an enclosed SKP chamber maintained at a constant 95% RH and 25  $^\circ\text{C}$ . Delamination was initiated on each occasion by introducing  $\sim 2 \text{ cm}^3$  of 0.86 M aqueous NaCl (pH 7) into the penetrative coating defect region. The SKP reference probe consisted of a gold wire of diameter 125  $\mu\text{m}$  vibrating vertically at 280 Hz and amplitude of 40  $\mu\text{m}$  at a distance of 100  $\mu\text{m}$  above the sample surface.  $\Delta\Psi$  data points were recorded at 20 per mm. The SKP reference probe was scanned over the coated surface along a 12 mm line normal to, and adjacent with, the defect-coating boundary. Scanning commenced immediately on the addition of electrolyte and thereafter at hourly intervals over a period of  $\geq 24$  h.

## 3. Results

### 3.1. SKP potentiometry

When iron or HDG zinc substrates coated with PVB or PVB-GNP were subject to SKP scanning in air at 95% RH the measured values of  $\Delta\Psi$  were found to be substantially uniform over the sample surface and became stable (time-independent) after approximately 2 h. Fig. 3 shows area-averaged (20 data points per millimetre over a length of 12 mm repeated 4 times and 1 mm apart) time-independent  $\Delta\Psi$  values plotted

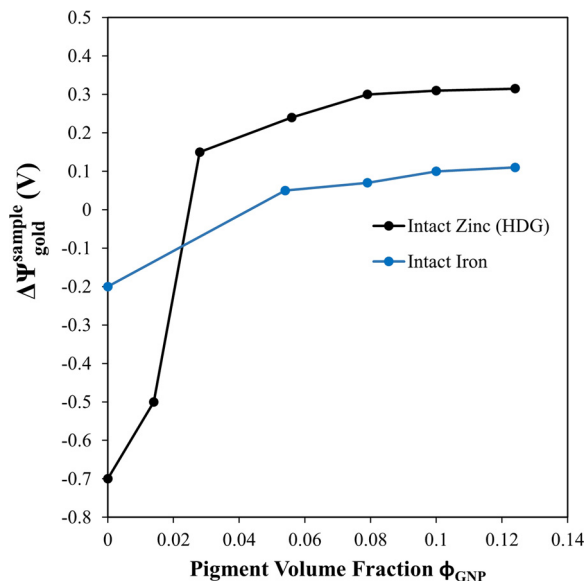


Fig. 3. A plot of the average time independent  $\Delta\Psi$  values measured for the intact region for each of the PVB and PVB-GNP coated samples against respective  $\phi_{\text{GNP}}$  for both iron and zinc (HDG) substrates.

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