Facile Corrosion Protection Coating from Graphene

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***Abstract*—Corrosion is a serious global problem, affecting our daily lives and causing million dollar lost in industry annually. Chemical reaction occurs when metal surface comes in contact with oxygen in air, resulting metals being oxidized and corroded. Various methods have been employed by the industries to protect metal from corroding, such as applying coating with paints and varnishes. However, each method has its own limitations, such as modification of the protected metal, thickness of the coating, altering the dimensions and conductivities of the metal and enormous cost involves in the coating process. Therefore, the challenge in developing a protection barrier from corrosion is to develop an economical yet efficient method for the coating material. In this project, we developed a cheap and facile method of coating metal surface with graphene layer for corrosion protection. Starting from common graphite powder, graphene coating was deposited onto copper plate via electrophoretic deposition (EPD) method. The deoxygenation of carbon was confirmed by bathochromic shifting in UV spectroscopy. Graphene protection layer was further characterized electrochemically via potentiodynamic polarization testing in chloride solution. Potentiodynamic polarization curves show the decrease of both corrosion potential (E_{corr}) and corrosion current (i_{corr}), suggesting graphene protection layer decreases the copper dissolution process.**

***Index Terms*—Electrophoretic deposition, graphene, corrosion.**

I. Introduction

The Noble Prize in Physics in 2010 was won by Andre K. Gein and Konstantin Novoselov for the "groundbreaking experiments regarding the two dimensional material graphene". Graphene, which is a single layer sheet of carbon atoms which are sp^2 hybridized and arranged in a honeycomb pattern, has attracted masses of attention due to its fascinating physical properties [1]. These include enhanced electronic conductivity, thermal stability and mechanical strength [2]. The interesting properties raise the possibilities of graphene being manipulated to be incorporated into a variety of applications which include ultracapacitor, solar cells, liquid crystal devices and transparent conducting films.

Graphene as a corrosion protection barrier is also one of the field which has generated interest among researchers. As graphene is chemically inert and stable under temperature up to 400°C, it would be a perfect candidate which can provide an anti rust protection layer. Graphene coating is believed to be able to suspend the transfer of charges at the metal surface without interfering with the electrical and optical properties of the coated surface. Chen *et al.* conducted a study on the oxidation resistance of graphene coated Cu and Cu/Ni alloy and it was confirmed that chemical vapor deposition (CVD) graphene layer works as a barrier for Cu and Cu/Ni alloy against air oxidation and chemical oxidation in the solution of 30% hydrogen peroxide [3].

Meanwhile, Kirkland *et al.* also conducted a study of graphene as a corrosion barrier on CVD grown graphene on nickel and copper sample [4]. Their result showed the possibility of CVD graphene as a layer of corrosion barrier. However, all the above mentioned graphene coatings were deposited via CVD which involve tedious and high vacuum system. Electrophoretic deposition (EPD) is a simple electrochemical method used to deposit thin layer of coating onto any conducting substrate. For the EPD of graphene layer, a dc electric is applied to the well dispersed graphene oxide solution, causing graphene oxide particles to migrate towards the electrodes and form a desired deposition on the electrode surface. This method is a well-developed and cost effective method which has advantages from many aspects such as its deposition rate, good thickness controllability, good uniformity and simplicity scale up [5]. An *et al.* studied on the anodic reduction of graphene oxide through electrophoretic deposition and reported a uniform layer of graphene can be deposited via this environmental friendly approach [6].

Manuscript received September 8, 2012; revised November 26, 2012.

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II. Experimental

A. Chemicals

All the chemicals used in this experiment were purchased from Sigma Aldrich unless otherwise stated and were used as received.

B. Graphene Oxide Preparation

20 g of graphite powder was added into a solution of concentrated H_2SO_4, $K_2S_2O_8$ and P_2O_5 at 80°C. The solution was stirred for 30 minutes before the heat was removed and it was cooled to room temperature for 6 hours. De-ionized water was then added into the solution and the mixture was filtered and washed until the filtrate turns to pH 7. The pre-oxidized graphite powder was then dried overnight. Next, dried pre-oxidized graphite powder was added into a 2 L of concentrated H_2SO_4 at 0°C, followed by $KMnO_4$. The addition process must be performed with stirring and the temperature must be maintained at < 20°C. The mixture was then heated to 35°C for 2 hours and the mixture will thicken up and effervescence paste in brownish grey color was obtained. 920 mL of deionized water was then added into the resulting mixture while maintaining the temperature at98°C for 15 minutes. This solution was then added into 2.8 L of de-ionized water. 50 mL of concentrated H_2O_2 was added and

this will turn the solution to bright yellow. The solution was washed with a 5 L diluted HCl (ratio 1:10 with DI water) and the produced graphite oxide was dried overnight. Graphene oxide solution was obtained by exfoliating graphite oxide solution using the ultrasonicator for 30 minutes. Graphene oxide will be denoted as GO.

C. Electrophoretic Deposition (EPD)

1.0 mg/mL GO solution was used as the electrolyte in EPD. Two copper strips (1 cm × 4 cm) were used as the electrodes, acting as anode and cathode respectively. The electrodes were placed vertically in a small beaker and they were separated 1 cm horizontally from each other. A direct current potential of 1 V was supplied by the PARSTAT 2273 potentiostat to the set up for 10 minutes. The samples were rinsed and dried in the drying cabinet overnight.

D. Characterization

UV analysis was done on GO solution and the Cu+G. The deposited graphene layer was scrapped off from copper surface and dispersed in DI water for UV analysis. For air oxidation, samples were heated at 200°C for 4 hours in the oven. For chemical oxidation, samples were immersed in a solution of 30% H_2O_2 for 2 mins. The area of the electrophoretic deposited and non-electrophoretic deposited samples were photographed before and after the oxidation process. For electrochemical testing, three-electrode system was used in 0.1 M NaCl solution. The samples were used as working electrode (area exposed = 1 cm^2), Ag/AgCl as reference electrode and Pt wire as counter electrode. Polarization curve was performed at -250 mV and +250 mV with respect to the open circuit potential (1 hour stabilization) at scan rate of 1 mV/s.

III. Results and Discussions

A dark layer was observed at the anode electrode after applying dc potential of 1 V for 10 minutes in GO solution. The loosely attached layer was removed during rinsing process and a thin and smooth layer was obtained on Cu+G surface as Fig. 1. The layer is strongly adhered to copper surface and remains intact even with mechanical rubbing.

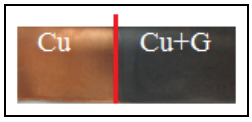

Fig. 1. Photograph of copper strip with electrophoretic deposited graphene (Cu+G).

UV-Vis spectroscopy was conducted in order to monitor the reduction process of GO into graphene as demonstrated by the bathochromic peak shifting. Fig. 2 shows the UV spectra of GO and Cu+G. The GO solution used as the electrolyte in the electrophoretic deposition (EPD) process displayed a peak at 232.7 nm and it can be attributed to the transition of □→□* transitions of the C=C double bond. Upon deoxygenation process, this peak will be red shifted as the electronic conjugation of graphene sheets is restored. It can be clearly seen from the Cu+G absorption spectrum. This red shift indicates that the electrophoretic deposition (EPD) process has notably removed the oxygen functional groups of GO.

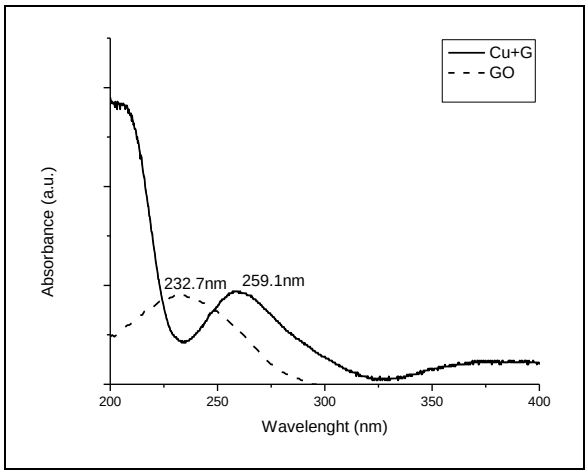

Fig. 2. UV-Vis spectra of GO and Cu+G.

UV analysis suggested that the GO was reduced at the anode electrode. However, this seems contradictory with the electrochemistry theory whereby oxidation occurs at the anode electrode. Therefore, the suggested electrochemical reactions as follow:

$RCOO^- \rightarrow RCOO\cdot + e^-$ (oxidation of carboxylate)

$RCOO^- \rightarrow R\cdot + \cdot CO_2$ (oxidation decarboxylation)

$2R\cdot \rightarrow R\text{-}R$ (dimerization of radicals)

Fig. 3 shows the photographs of Cu+G copper strips after chemical oxidation with H_2O_2 and air oxidation at 200 ℃. It can be clearly seen that little changes could be observed at the Cu+G layer while tremendous changes can be seen on bare copper area. It shows that the bare copper area underwent the oxidation process in both chemical and air oxidation processes. Cu+G provides a layer of protection barrier to the copper surface beneath the coating and prevents the metal surface from coming in contact with the oxidizing agents such as peroxides ions and oxygen.

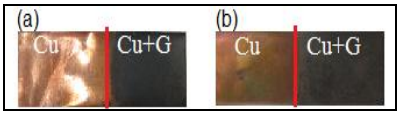

Fig. 3. Photographs of Cu+G copper strips after (a) chemical oxidation with H2O2 ; (b) air oxidation at 200 ℃. (Chemical oxidation and air oxidation were conducted on difference Cu+G copper strips.

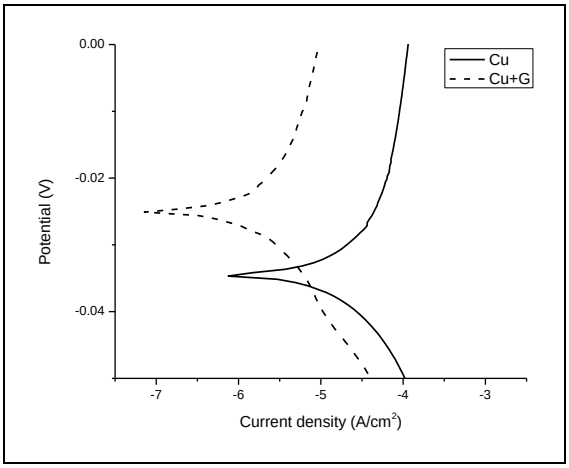

Fig. 4. Polarization curves of bare copper and Cu+G.

Fig. 4 shows the polarization curve for the bare copper and Cu+G samples. The polarization curve enables the corrosion potential and the current densities, i_{CORR} to be determined and compared between the graphene coated and uncoated copper sample. The corrosion potential, E_{CORR} is a measurement of sample resistance towards corrosion. From the polarization curve, it can be seen that there is a shift in the E_{CORR} towards the positive direction for the Cu+G sample. It proves the graphene coating acts as a corrosion resistance barrier. Meanwhile, the current densities enable the oxygen reduction reaction rate to be determined. As seen in the polarization curve, current density of the Cu+G is lower than the current density of the bare copper. The decrease in the current densities rate proves that the graphene coating acted as a barrier to the underlying copper surface and hence, decreased the copper dissolution and hence reducing corrosion rate.

IV. Conclusion

In summary, this project demonstrates a simple and direct method of depositing graphene layer onto copper surface by electrophoretic deposition process. The electrodeposited graphene layer offers excellent protection against air and chemical oxidation as well as corrosion. The electrodeposited graphene layer adheres strongly onto the substrate and holds promising applications in corrosion protection industry.

Acknowledgements

KF Chong and coworkers would like to thank the funding support of RDU110352 and RDU121213.

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