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Electrodeposition and corrosion behavior of Sn and Sn-reduced graphene oxide coatings on mild steel from the non-cyanide acid chloride bath solution

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Abstract

Reduced graphene oxide (rGO) derived from graphite has received attention among researchers because of its special unique characteristic properties. Based on the studies, rGO-based coatings on stainless steel (SS) act as an anti-corrosive protective coating on stainless steel. Herein, we prepared a few layered rGO via graphite oxide by a simple thermal exfoliation of graphite oxide. Tin and Sn-rGO coatings have been electrodeposited on SS using an optimized acid chloride bath composition in the absence and presence of rGO respectively. The prepared specimens were subjected to an aggressive corrosive environment (aqueous 5% NaCl). The corrosion behavior of Sn and Sn-rGO composite coating has been examined by potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) techniques.

The potential shifted towards the negative region after polarization for Sn-rGO composite coating compared to pure Sn coating. Also, Sn-rGO composite coating exhibits more resistance when subjected to EIS measurements in 5% NaCl. The change in the surface morphology of coatings before and after exposure to corrosive environments has been observed by Scanning electron microscopy. After exposure to aqueous 5% NaCl, Sn coated specimen exhibited pores on the SS surface whereas fewer pore structures were observed on the SS surface for Sn-rGO coating. The results reveal a significant increase in anti-corrosion properties of Sn-rGO on SS compared to that of pure Sn coating.

Keywords: Tin, Reduced graphene oxide, Sn-rGO coatings, Corrosion resistance.

Introduction

Steel is world's most important engineering and construction material due to its low cost, abundant availability in the earth's crust and outstanding properties[21]. However, steel easily undergoes corrosion when it is exposed to the open atmosphere which leads to many safety issues which cause heavy economic losses for the nation and society. Therefore, the protection of steel from corrosion remains one of the big challenging issues for researchers. The sacrificial behavior of an electroplated metal coating is widely used to protect steel from corrosion[11,21,27,28]. There are many methods used to produce sacrificial coatings to protect the base metal.

Based on the applications, the researchers tried to protect the steel metal by coating it with metals such as zinc, nickel, manganese and tin using an electrochemical deposition technique[2,27-29]. However, the durability of metal-coated articles is limited due to the quick dissolution of metal under aggressive environments and it forms white rust on the steel article[2,29]. Alternatively, to improve the life span and anti-corrosion properties of steel, the sacrificial metal or carbon-based metal composites modification is required. It is known that a small quantity of carbon-based material can enhance the anti-corrosion properties of steel. Coating with carbon-based materials such as carbon nanotubes[2,19], graphene oxide[20] and graphene[15] has provided better protection of base metal as well as sacrificial metal coating[2,15,18-20,29].

Currently, Sn is extensively used in coating beverage cans and in food packaging[8]. Many researchers reported on the electrodeposition and corrosion protection of Sn and Sn-based composite coatings. It has been proved that carbon-based tin composite coatings exhibit good corrosion resistance[7,8,12], excellent solderability[1,23], good ductility[6,33], no toxicity[13] and smooth morphology[24]. Thus, Sn-based coatings are used in many domains such as marine industries[8], the automobile industry[12,33], microelectronics[14], aeronautics[34] and food industry[22].

Graphene is wonder material that attracted researchers considerably because of its superior properties which include electrical, thermal, conductivity, mechanical, hydrophobic and good flexibility[32]. It has been proved that a small quantity of graphene as an additive material can enhance the anti-corrosion properties of the base metal[3,32]. The unique nanoscale nature of graphene-based composite materials can provide improved anti-corrosive properties to the base metal under aggressive corrosive medium[2,15,19,20,29].

Furthermore, single-layered graphene provides excellent anti-corrosion ability to steel[2,19]. The incorporation of a small quantity of graphene into the zinc matrix can hinder the course growth of zinc which leads to the formation of nanocrystalline zinc deposits improving the corrosion resistance of steel substrate[20]. Recently, few researchers

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have reported on graphene-modified zinc and nickel-rich composite coatings to enhance the anti-corrosion properties of steel[2,19,20,25,26]. Graphene and reduced graphene prepared by many methods have been reported in the literature[30]. Of these methods, thermal exfoliation at low-temperature is better for producing reduced graphene oxide in bulk at a low cost[26]. It has been reported that the insertion of a few layered reduced graphene oxide to metal matrix protects the base metal under corrosive environments[10,31].

Based on the studies, the traditional metallic coatings were used to protect the corrosion[9,17]. It has been well established that the insertion of a small quantity of graphene into the metallic matrix enhances considerable anti-corrosion properties[15,16]. Recently, we reported improved anti-corrosion behavior exhibited by Ni-reduced graphene oxide (Ni-rGO)[5] and Zn-reduced graphene oxide (Zn-rGO)[4] based composite coatings over pure Ni and Zn coatings. The improved anti-corrosive property of Ni-rGO and Zn-rGO composite coatings on steel is primarily due to the addition of the small amount of rGO which decreases the formation of pits in the coatings and changes the morphology and texture of the coatings[15,16].

In the present study, a few-layered rGO nanosheets were synthesized by low-temperature exfoliation of graphite oxide using a modified Hummer's method[26]. The produced few layered rGO nanosheets were used to prepare tin-reduced graphene oxide (Sn-rGO) composite coatings on mild steel substrates. The electrodeposited Sn and Sn-rGO composite coatings have been tested in 5% NaCl solution. The electrochemical measurements suggested that the insertion of a small quantity of rGO enhanced the anti-corrosion properties of the Sn-rGO coating over pure Sn coating.

Material and Methods

Preparation of reduced graphene oxide (rGO): Graphite oxide (GO) was prepared by modified Hummer's method[26]. In the typical synthesis, concentrated H_2SO_4 (92mL) was taken in a 500mL conical flask and kept in the ice bath to maintain a low temperature. Graphite powder (2g) and $NaNO_3$ (2g) were added to the above solution followed by slow addition of 6g of potassium permanganate with continued stirring for 2h. The above mixture was diluted with slow addition of 92mL distilled water followed by careful addition of 100mL of 30% H_2O_2. The prepared GO was washed with 5% HCl followed by distilled water until no sulfate in the filtrate was detected. Finally, the solid cake was separated and dried at 100ºC in a vacuum oven for 24h. A few layered rGO was prepared by keeping the GO sample in a preheated furnace (200ºC) under an air atmosphere. The obtained layered rGO was removed carefully from the furnace and used for the preparation of Sn-rGO composite coatings.

Electrodeposition of tin and Sn-rGO composite coatings: Pure tin and Sn-rGO composite coatings were obtained by electrodeposition technique using acid chloride bath solution[1]. Two mild steel plates of equal area were used as cathode and anode. Before being subjected to electroplating, SS plates were polished using different grade of emery paper. The SS plates were washed with 10% NaOH followed by clean water. Finally, the mild steel plates were activated by dipping in 10% HCl for about 2-3 minutes.

The electrolyte was prepared by dissolving 9.2 gL^{-1} of $SnCl_2$, 26.7 gL^{-1} of NH_4Cl, 30.9 gL^{-1} of H_3BO_3 and 43.6 gL^{-1} of sodium gluconate in distilled water. A current density of 6.5 $mAcm^{-2}$ was applied for 20 min to tin and Sn-rGO coatings on the mild steel substrate. The pH of the solution was maintained at 3.5. The deposition was carried out at room temperature under continuous stirring at 100 rpm. The Sn-rGO composite coating was prepared from the Sn plating bath into which 0.05 gL^{-1} of graphene was dispersed. All other deposition parameters were kept constant. The rGO present in the electrolyte was uniformly dispersed by continuously stirring at 300 rpm for 5 hrs. The schematic representation of tin and Sn-rGO deposition is shown in figure 1.

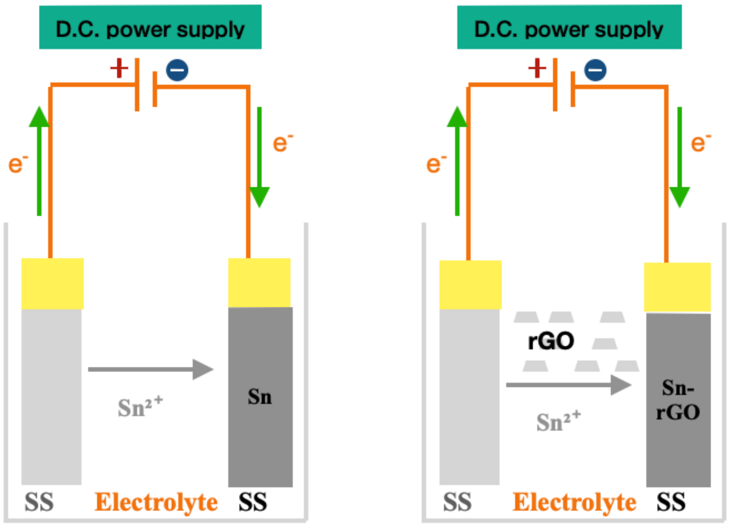

Fig. 1: Schematic diagram for electrodeposition for Tin(a) and Sn-rGO (b) composite coatings

Results and Discussion

X-ray diffraction patterns of GO and rGO are shown in figure 2(a). The diffraction peak at 10.6^{o} corresponds to GO and the characteristic diffraction peak for rGO prepared by thermal exfoliation of GO at 200^{o}C was observed at 24.4^{o} indicating the formation of rGO. Figure 2(b) represents the SEM image for rGO. It is clearly seen from the figure that there are few-layered graphene oxide stacks obtained after thermal exfoliation[26].

The effect of rGO on crystal growth during the electrodeposition of Sn-rGO coatings is further carefully observed in Scanning electron microscopy (SEM). Figures 3a and 3b depict the SEM micrographs for tin and Sn-rGO coatings respectively. The crack-free morphology was observed in both pure tin and Sn-rGO coatings. A pure tin-coated sample electrodeposited in the electrolytic bath solution in the absence of rGO has a relatively smooth and regular surface.

However, upon the addition of rGO in the electrolytic bath solution, excellent change in the surface morphology of the tin coating exhibited the surface with a small quantity of rGO-grown clustered structure. It has been reported that the addition of rGO during electrodeposition can hinder crystal growth and can increase the nucleation sites for the reduction of metal ions[6,23]. The above factor may be the reason for the change in morphology and size of tin crystals of the Sn-rGO composite coatings.

Figures 4a and 4b show images correspond to pure tin and Sn-rGO coatings after polarization measurements carried out in an aqueous 3.5% NaCl aggressive corrosive electrolyte medium respectively. After polarization, the dissolution of tin with the formation of pits (Fig. 4a) on the surface of the pure tin coating was observed. However, minimal dissolution of tin and pits was observed in the presence of rGO in Sn-rGO coating. The SEM images confirm that Sn-rGO composite exhibits higher corrosion resistance under 3.5% NaCl aggressive corrosive medium.

The corrosion resistance property of pure Sn and Sn-rGO composite coatings was studied by the potentiodynamic polarization measurements carried out in 3.5% NaCl solution. Electrochemical corrosion measurements were performed for pure Sn and Sn-rGO coatings as shown in figure 5. Tafel curves were obtained whose measurements were made by polarizing the working electrode to 200mV against the open-circuit voltage at the scan rate of $20mVs^{-1}$. The polarization curve for Sn-rGO composite coating was shifted to higher polarization potential and lower current density region in comparison with that of the pure Sn coating which inferred that the incorporation of rGO leads to the change in the corrosion resistance of the pure tin coating.

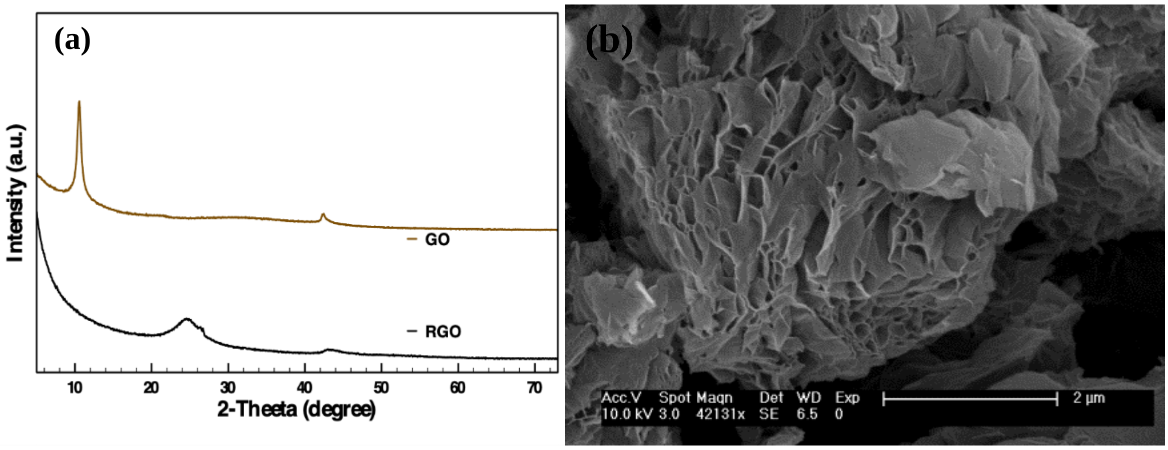

Figure 2: (a) X-ray diffraction patterns of GO and rGO (b) SEM image for rGO

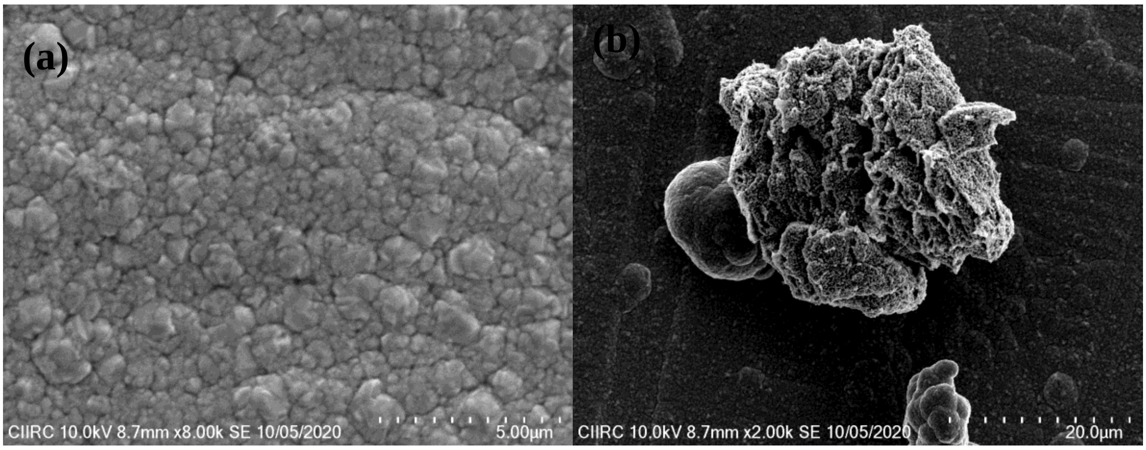

Figure 3: Scanning electron micrographs of (a) Tin and (b) Sn-rGO composite coatings

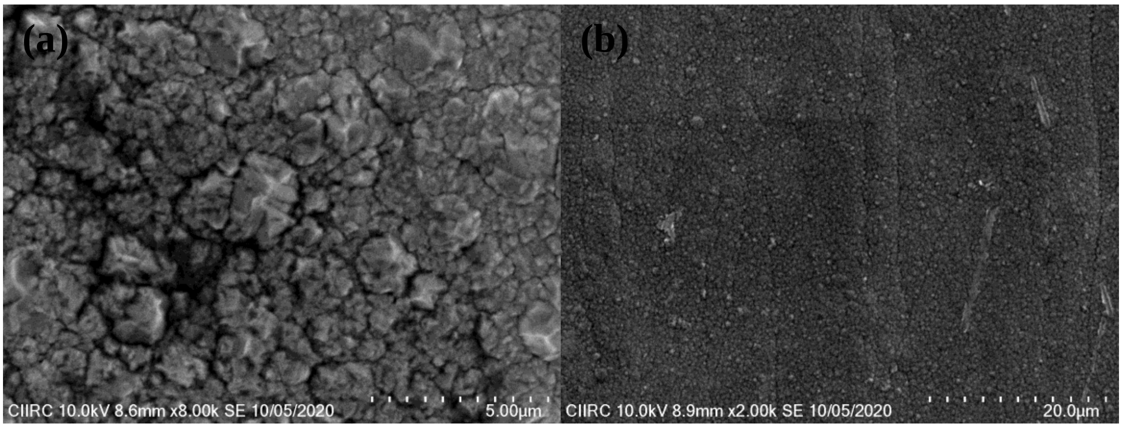

Figure 4: Scanning electron micrographs of (a) Tin coating and (b) Sn-rGO composite coatings after polarization in 3.5% NaCl.

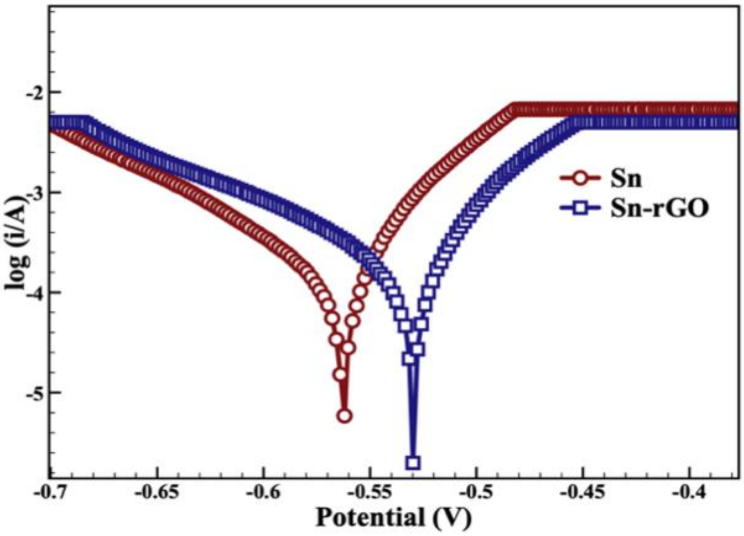

Figure 5: Potentiodynamic polarization curves for Sn and Sn-rGO composite coatings recorded in 3.5% NaCl media against Ag/AgCl reference electrode

The corrosion potential (E_{corr}) values for pure tin and Sn-rGO coatings were -0.562V and -0.529V respectively. This result reveals that the rGO-incorporated tin coating required more potential to release electrons compared with the pure tin coating[1]. It is well known that compared with the corrosion potential, the corrosion current density is a more concluding parameter in evaluating the corrosion resistance of coatings. A significant reduction in the corrosion current density for the Sn-rGO composite coatings in comparison with the pure tin coating strongly reveals that the incorporation of rGO can improve the corrosion resistance of the tin coating.[1,16]

The electrochemical impedance measurements (EIS) were carried out to further explore the corrosion property of pure tin and Sn-rGO composite coatings in a 3.5% NaCl solution. The EIS measurements were carried out at an open circuit potential value corresponding to a working electrode in the frequency range of 100kHz to 10MHz with a sinusoidal signal amplitude of 5mV. The measured EIS data for pure tin and Sn-rGO coatings were presented as a Nyquist plot in fig. 6(a). It can be clearly seen that the Nyquist plots for both the pure Sn coating and Sn-rGO composite coatings exhibit a non-well-defined semicircle-shaped capacitive loop.

Similar impedance spectra with a small tail were reported on the corrosion behavior of the pure tin and that of Sn-rGO coatings[1,16]. The measured length of the capacitive loop which is a measure of polarization resistance, is higher for the Sn-rGO composite coating and lower for the pure tin coating. These results reveal that the Sn-rGO composite coatings exhibit better corrosion resistance than that the pure tin coating. Moreover, the size of the capacitive loop for these Sn-rGO composite coatings is also different which implies different corrosion resistance behaviors.

To evaluate quantitatively the corrosion resistance behavior and calculate the corrosion parameters, the EIS fitted data are expressed using an equivalent circuit by the circuit model $\{R_s(CPE_1(R_1(CPE_2\ (R_2))))\}$ shown in fig. 6(b). Since all the recorded EIS spectral data do not have a purely capacitive character, a constant phase element (*CPE*) was used to represent the capacitor element for better-quality fitment and the formula for calculating the impedance of the *CPE* was obtained from the literature[1,15].

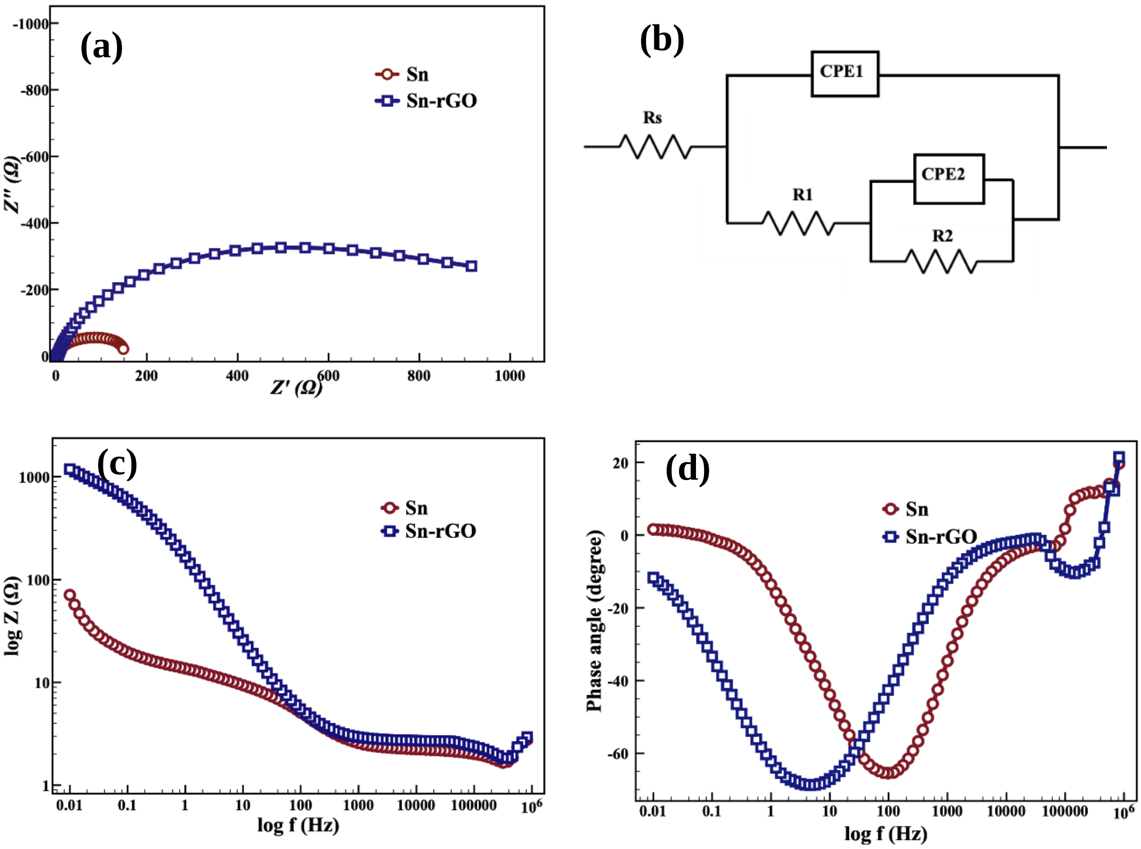

Figure 6: Electrochemical impedance measurements for Tin and Sn-rGO composite coating measured in 3.5% NaCl solution against Ag/AgCl reference electrode

In the equivalent circuit, *Rs* represents the solution resistance between the reference electrode and the surface of the working electrode. R_1 and CPE_1 represent the resistance and capacitance of the coatings respectively. R_2 and CPE_2 represent the charge transfer resistance and double-layer capacitance at the interface of the working electrode and the solution[1,15]. The total polarization resistance (R_p) is the sum of the coating resistance and charge transfer resistance and it can be used to evaluate quantitatively the corrosion resistance performance of the coatings[1]. It can be seen that the R_p of Sn-rGO is ten times higher than that of the Sn coating (147Ω). Furthermore, the Sn-rGO composite coating attained from the electrolyte containing rGO exhibits a maximum R_p value of about 915Ω. This is in good agreement with the results obtained from the potentiodynamic polarization tests, indicating that the Sn-rGO composite coating provides higher corrosion protection to the steel substrate than that of the pure tin coating[1,15].

Additionally, the corrosion resistance properties of tin and Sn-rGO coatings were analyzed from the Bode impedance plots [Fig. 6(c) and 6(d)] i.e. log Z and phase angle versus log frequency plots. It can be clearly seen from figure 6c, that the addition of rGO to tin coating in Sn-rGO coating increases impedance value and thereby increases resistance of the coating. Moreover, in figure 6(d), the phase angle increased at the low-frequency region for the Sn-rGO coating and decreased at the high-frequency region for pure tin coating. The shift in the higher angle at lower frequency region for the Sn-rGO coating is due to reduced surface area to corrosive medium and the formation of a barrier layer between the electrode and corrosive medium[1,16]. The overall result indicates that adding a small quantity of rGO to tin coatings increases the corrosion resistance of the tin coating.

Conclusion

Sn and Sn-rGO coatings were successfully deposited on mild steel by direct current from an acid sulfate bath at 298 K. The Sn-rGO coating was prepared in the presence of reduced graphene oxide sheets. The rGO nanosheets were deposited along with the tin on the mild steel surface. The incorporation of rGO changed the structure and morphology of the tin coatings. The electrochemical corrosion studies revealed that the Sn-rGO coatings significantly increased the corrosion resistance than that of the pure tin.

Sn-rGO coatings provide a physical barrier to the corrosion medium by rGO filling in the active micro-sites on the mild steel surface and hence it reduces metal dissolution. Also, the results show that rGO plays an important role in the formation of Sn-rGO coatings by controlling the deposition of tin metal on mild steel.

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