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## Corrosion and biodegradability evaluation of magnesium substituted porous hydroxyapatite/polyethylene dioxy thiophene bilayer coating on 316l stainless steel for orthopaedic applications

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**Abstract :** Surgical grade stainless steel (316L SS) is a widely used biometallic implant material in orthopedic applications. The need to reduce costs in public health services has compelled the use of 316L SS as the most economical alternative for orthopedic implants. However, the release of metallic ions is evident from the biometallic implant in physiological solution. For this reason, it is essential for developing bilayer coatings to improve the corrosion resistance and bioactivity of 316L SS. Conducting polymers are used as surface coatings to protect metals against corrosion and moreover it is an environment friendly and effective method. The present study deals with the successful development of bilayer coatings by electropolymerisation of polyethylene dioxy thiophene (PEDOT) on 316L SS followed by the electrodeposition of magnesium (Mg) substituted hydroxyapatite (Mg-HA). The bilayer coatings were characterised by Fourier transform infrared spectroscopy, high resolution scanning electron microscopy, energy dispersive X-ray analysis. The corrosion resistance of the obtained coatings was also investigated in Ringer's solution by electrochemical techniques such as potentiodynamic polarisation and electrochemical impedance spectroscopy. Thus, the PEDOT/Mg-HA bilayer coated 316L SS can serve as a prospective biomaterial for orthopaedic applications.

**Keywords:** 316L SS; Polyethylene dioxy thiophene; Substituted hydroxyapatite; Electrochemical impedance spectroscopy, Polarisation.

### Introduction

Among various bioimplant materials, 316L SS is widely used in orthopaedic and dental implant applications owing to its low cost, good biocompatibility, excellent mechanical properties and ease of fabrication<sup>1</sup>. But the formation of chromium oxide passive layer on the 316L SS surface was unable to tolerate

with the physiological environment and hence the release of metallic ions such as chromium, iron and nickel are evidenced in the human body. Therefore, the surface treatment for the 316L SS specimens is necessary to prevent the release of metallic ions in physiological solution<sup>2</sup>. Moreover, since the 316L SS are not bioactive, in order to ensure the corrosion resistance and bioactivity of these kinds of materials, the surface of the 316L SS implants are usually treated with osteoconductive materials such as calcium phosphate bioceramics. Among these bioceramic materials, hydroxyapatite [HA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] is the most commonly used calcium phosphate based biomaterial for coating metallic implants and is most investigated during the previous decade and it has excellent bioactivity, similar structure and composition to human hard tissues. Also, HA in bone is a multi-mineral substituted calcium phosphate materials with the traces of magnesium ( $\text{Mg}^{2+}$ ), strontium ( $\text{Sr}^{2+}$ ), silicon ( $\text{Si}^{2+}$ ), carbonate ( $\text{CO}_3^{2-}$ ), barium ( $\text{Ba}^{2+}$ ) and Zinc ( $\text{Zn}^{2+}$ ) etc<sup>3</sup>. The biological properties of the HA based biomaterials might be enhanced by the addition of divalent and trivalent ions that has stimulated a number of studies on ion- substituted or doped HA coatings to induce favourable biological effects.

In particular, the advantageous effect of manganese ( $\text{Mn}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), strontium ( $\text{Sr}^{2+}$ ), silicon ( $\text{Si}^{2+}$ ), carbonate ( $\text{CO}_3^{2-}$ ), Cerium ( $\text{Ce}^{3+}$ ) and Yttrium ( $\text{Yt}^{3+}$ ) in HA based bioceramic coatings deposited on metallic substrates has been demonstrated<sup>4</sup>. These divalent and trivalent metal ion substitutions play an essential role in the bone formation and also affect bone mineral characteristics, such as bioactivity, mechanical properties and degradation behavior<sup>3</sup>.

$\text{Mg}^{2+}$  is a desirable and topical divalent ions for substitution into HA and is closely associated with the mineralization of calcified tissues, in particular during the early stages of osteogenesis where its depletion causes bone loss and bone fragility, and stimulates osteoblast proliferation with an effect comparable to that of insulin. Enamel, bone and dentin contain 0.44, 0.72, 1.23 wt% of  $\text{Mg}^{2+}$ , respectively. In regard to the above points, Mg substituted HA is expected to have better bioactivity than pure HA<sup>5,8</sup>.

A number of coating technologies are available for the development of bioactive coatings onto metallic implants. Such as dip coating, pulsed laser deposition, plasma spraying, electrochemical deposition, micro-arc method, electrophoretic etc. The electrochemical deposition has gained considerable attention because of the advantages in the coating fabrication such as low deposition temperature, process simplicity, the capability of forming an uniform coating on porous substrate (or) complex shapes of substrate and the availability and low cost of equipments. Recently have achieved the electrodeposition of porous substituted HAP coating on polypyrrole coated 316L SS and the coatings exhibited uniform morphology with desired structure<sup>3</sup>.

Based on the above advantages of electrodeposition, our present work was focused on the electrodeposition of porous Mg substituted HA (Mg-HA) on 316L SS for improved bioresistivity and biological properties. Though the coating of Mg-HA on 316L SS can improve the bioactivity, the component metallic ions of the 316L SS substrate may be oxidised and will release toxic metal ions through pores. Moreover, it has been reported that the bonding between the metallic substrate and substituted HA coating is very poor<sup>3,4</sup>. Therefore, in order to prevent leach out through pores and also to enhance the adhesion of Mg-HA with the substrate a conducting polymeric coating has been used in the present work.

PEDOT is one of the most gifted conductive polymers due to its numerous advantages such as such as excellent environmental stability, high conductivity, corrosion protection etc., Moreover, PEDOT has been investigated in many biomedical applications, because of its excellent biocompatibility and high aqueous stability<sup>9,10,11</sup>.

The main aim of our work is the development of porous Mg-HA coating on PEDOT coated 316L SS. Here, the first layer, i.e., PEDOT coated 316L SS may prevent the release of toxic ions thereby enhancing the adhesion strength between the Mg-HA coating and the 316L SS substrate and thus improves the corrosion resistance. The second layer, i.e., Mg-HA coating which is porous in nature and the interconnected pores can allow the attachment and proliferation of diverse cell types responsible for the formation of a functional tissue or organ. So, it is aimed to evaluate the corrosion resistivity and bioactivity of the as-formed bilayer coatings. Hence the present work is designed to achieve PEDOT/Mg-HA bilayer coating on 316L SS with improved adhesion strength, corrosion resistance and biological properties.

## Experimental

### Preparation of 316L SS samples

316L SS samples (elemental composition (wt%): C – 0.0222, Si – 0.551, Mn – 1.67, P – 0.023, S – 0.0045, Cr – 17.05, Ni – 11.65, Mo – 2.53, Co – 0.136, Cu – 0.231, Ti – 0.0052, V – 0.0783, N – 0.0659 and rest Fe) obtained from steel Authority of India Ltd., Salem, with dimensions of  $10 \times 10 \times 3$  mm<sup>3</sup> were used as the substrate materials in the present study. Before the electrodeposition process, all the 316 SS samples were abraded using different grades of silicon carbide (SiC) sheets (600, 1000 upto 2000 grit) to obtain homogeneous roughness. After grinding the samples, they were ultrasonically cleaned with deionized water, anhydrous ethanol and acetone for 10 min, in order to remove surface residues. After polishing, the cleaned specimens were dried under air pressure steam for 15 min and then used for further studies<sup>1-4</sup>.

### Chemicals

Commercially available ethylene dioxy thiophene, sodium salicylate, calcium chloride dihydrate (CaCl<sub>2</sub>.2H<sub>2</sub>O, 99.9% purity, Sigma–Aldrich, USA), magnesium chloride hexahydrate (MgCl<sub>2</sub>.6H<sub>2</sub>O, 99.8% purity, Sigma–Aldrich, USA), diammonium hydrogen phosphate ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, 99.9% purity, Sigma–Aldrich, USA) were used for the development of PEDOT/Mg-HA bilayer coatings by electrodeposition. Deionized water was employed as the solvent throughout the experiments and also the chemicals used were of analytical grade reagents which are used without further purification.

### Electrodeposition

#### Mg-HA coating on 316L SS

The electrolyte for Mg-HA deposition was prepared by dissolving a known amount of analytical grade 0.45 M CaCl<sub>2</sub>.2H<sub>2</sub>O, 0.05 M MgCl<sub>2</sub>.6H<sub>2</sub>O and 0.3 M (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> were dissolved in deionized water in the appropriate molar ratio to produce the target (Ca + Mg)/P ratio of 1.67. The electrolyte was de-aerated with N<sub>2</sub> for 30 min during the electrodeposition process in order to reduce the amount of dissolved carbon dioxide (CO<sub>2</sub>) and thus to minimize the formation of calcium carbonate (CaCO<sub>3</sub>) deposits. The pH of the electrolyte was adjusted to 4.5 using NH<sub>4</sub>OH and the temperature was maintained at 65 °C using thermostat. To keep the uniform concentration of the electrolyte solution, the magnetic stirring was controlled at a speed of 180 rpm for 3 h<sup>12</sup>.

In the present work, we have deposited porous Mg-HA on 316L SS at current density of 9 mA cm<sup>-2</sup> for the duration of 30 min which has been proved as the best current density to produce uniform porous coating on implant<sup>3,4</sup>. After the coating process, the coated specimens were removed from the electrolyte and gently rinsed with deionised water at room temperature for 4 h.

#### *PEDOT coating on 316L SS*

The electropolymerisation of ethylene dioxy thiophene on 316L SS was carried out in a regular three electrode system by galvanostatic method using an electrochemical instrumentation (CHI 760C (CH Instruments, USA)) in which the saturated calomel electrode (SCE), 316L SS and platinum electrode served as the reference, working and counter electrodes, respectively. The polymerisation of ethylene dioxy thiophene on 316L SS was performed in 0.2 M ethylene dioxy thiophene containing 0.5 M of sodium salicylate solution<sup>3,4</sup>. The applied potential was scanned between -0.5 V and +2 V vs SCE for 10 cycles at a fixed scan rate of 20 mV/s. All the potentials in this work are quoted on the SCE scale.

#### Mg-HA coating on PEDOT coated 316L SS

The same procedure was adopted for the coating of Mg-HA (at constant current density of 9 mA cm<sup>-2</sup>) as a second layer on the PEDOT coated 316L SS. After the electrodeposition process, the PEDOT/Mg-HA bilayer coated 316L SS samples were gently rinsed with deionised water and then dried for 24 h.

#### *Surface characterisation of the bilayer (PEDOT/Mg-HA) coating*

The Fourier transform infrared (FT-IR) spectra of the PEDOT/Mg-HA bilayer coated 316L SS samples were recorded using Nicolet 380 FT-IR Spectrometer (Perkin Elmer, USA) over the frequency range from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> with a number of 32 scans and spectral resolution of 4 cm<sup>-1</sup>. The morphological features and

elemental composition of the as-deposited bilayer coatings were examined using scanning electron microscopy equipped with energy dispersive X-ray analysis (SEM/EDX) (JEOL JSM-6400, Japan).

### Adhesion tests

The adhesion strength can suggest expensive information on the mechanical properties of the surrounding bioceramic coating and metallic implant. Adhesion strength of the PEDOT, Mg-HA and PEDOT/Mg-HA bilayer coatings on 316L SS specimens were studied by pull-out test according to the American Society for Testing Materials (ASTM) international standard F1044, with at least five measurements for each coated samples. All the samples were cured in an oven at 100 °C during 30 min and were subjected to tests at a constant crosshead speed of 1 mm/min<sup>13</sup>.

### Electrochemical investigation of the coatings

In this study, potentiodynamic polarization was carried out in Ringer's solution (NaCl-8.6 g/L, CaCl<sub>2</sub>.2H<sub>2</sub>O-0.66 g/L and KCl 0.6 g/L) to assess the corrosion resistance of uncoated and as-coated 316L SS samples. The pH of the electrolyte was maintained at 7.4 and the temperature was kept at 27 ± 1 °C and also the solution was refreshed every day.

The electrochemical studies were performed using a three-electrode system (CHI 760C, USA) in which 316L SS specimen with an exposed surface area of 1 cm<sup>2</sup> were used as the working electrode, SCE and platinum as the reference and counter electrode. Potentiodynamic polarization studies were performed in a potential range of -1000 mV to -1000 mV vs. SCE with scan rate of 0.1 mV s<sup>-1</sup>. The potentiodynamic polarization was repeated at least three times to ensure for the reliability and reproducibility.

## Results and discussion

### Electropolymerisation of ethylene dioxy thiophene on 316L SS

The electropolymerisation of ethylene dioxy thiophene on 316L SS was performed in 0.2 M ethylene dioxy thiophene containing 0.5 M of sodium salicylate solution by using cyclic voltammetry (CV) at a fixed scan rate of 20 mV s<sup>-1</sup> and for 10 cycles in the potential range between -0.5 V and 2 V (vs. SCE). The cyclic voltammogram (CV) for PEDOT coating on 316L SS is shown in Fig. 1. The anodic peak observed at 0.9 V (vs. SCE) was attributed to the electropolymerisation of ethylene dioxy thiophene as well as the oxidation of sodium salicylate forming a passive film underneath the PEDOT coating of 316L SS specimen. Separate peaks cannot be detected owing to overlapping of oxidation peaks of ethylene dioxy thiophene and sodium salicylate. With the increasing cycle numbers upto 10 cycles, a slight increase in current density was observed at the end of each cycle while the decrease of intensity of oxidation peak of ethylene dioxy thiophene.

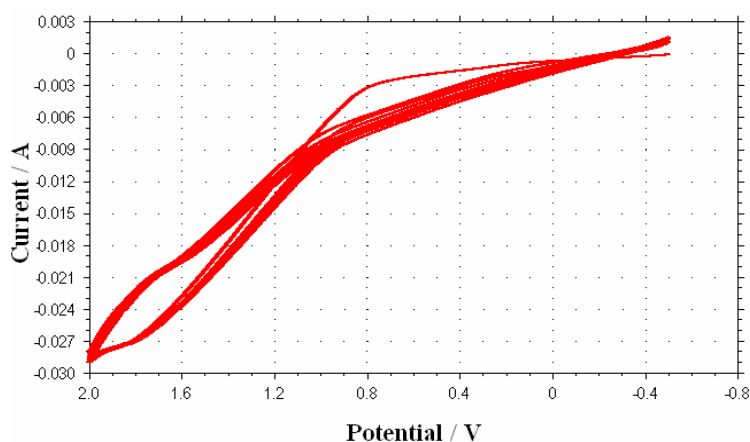


Fig. 1. Cyclic voltammogram for PEDOT coating on 316L SS.

The drop of the peak intensity is a result of ethylene dioxy thiophene being involved in the passivation process and the decrease in current intensity continues the cycles. The slight increase in current at the end of each cycle is due to the development of ethylene dioxy thiophene oxidation that occurs in a step by step manner which leads to the growth of PEDOT layer with increasing thickness on 316L SS sample<sup>3,4</sup>.

### Structural characterizations of the coating

#### Fourier transforms infrared spectroscopy

The FT-IR spectrum of the PEDOT/Mg-HA bilayer coated 316L SS sample is shown in Fig. 2. The characteristic peaks  $1017\text{ cm}^{-1}$  ( $\nu_3$ ),  $595\text{ cm}^{-1}$  &  $559\text{ cm}^{-1}$  ( $\nu_4$ ),  $474\text{ cm}^{-1}$  ( $\nu_2$ ) as well as the bands located at  $1080\text{ cm}^{-1}$  ( $\nu_3$ ) and  $948\text{ cm}^{-1}$  ( $\nu_1$ ) are ascribed to the phosphate groups. The broad band at  $1635\text{ cm}^{-1}$  is derived from the  $\nu_2$  bending mode and the band at  $3441\text{ cm}^{-1}$  depict the stretching mode of the hydrogen-bonded water molecules<sup>4</sup>.

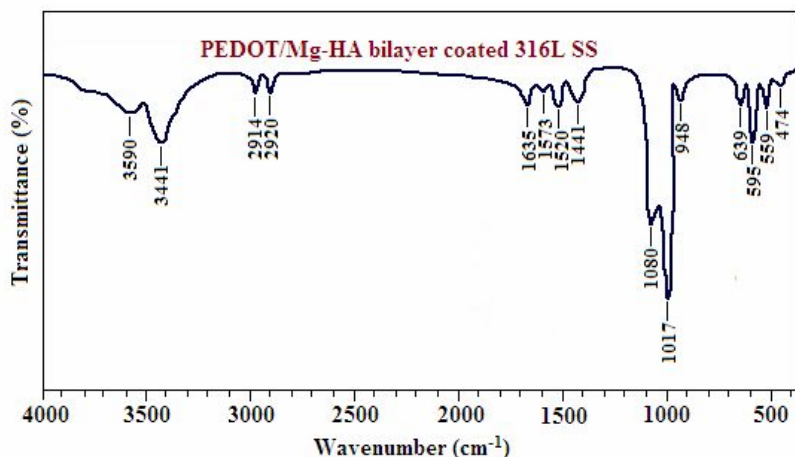


Fig. 2. The FT-IR spectra of bilayer PEDOT/Mg-HA coated 316L SS.

The stretching and bending modes of the hydroxyl groups of Mg-HA appear at  $3590$  and  $639\text{ cm}^{-1}$ , respectively. Apart from these, the peaks located at  $1441$ ,  $1520$  and  $1573\text{ cm}^{-1}$  are due to the stretching vibration of C=C, C-C and C-S-C group in the ethylene dioxy thiophene ring, respectively. Further, the peak located at  $1635\text{ cm}^{-1}$  is owing to the formation of metal-salicylate complex<sup>4</sup>. All the above said peaks are found for both PEDOT and Mg-HA as presented in Fig. 2 which strongly reveals the formation of PEDOT/Mg-HA bilayer coating on 316L SS specimen.

#### Scanning electron microscopic investigations

The Fig. 3(a-c) shows the HRSEM images of the PEDOT, Mg-HA and PEDOT/Mg-HA bilayer coatings on 316L SS. It can be seen in Fig. 3(a) that the coating exhibited the formation of granular and uniform microstructure of PEDOT coating on 316L SS. The morphological feature of as-deposited Mg-HA coating on 316L SS is shown in Fig. 3(b) which exhibits the interconnected porous network microstructure.

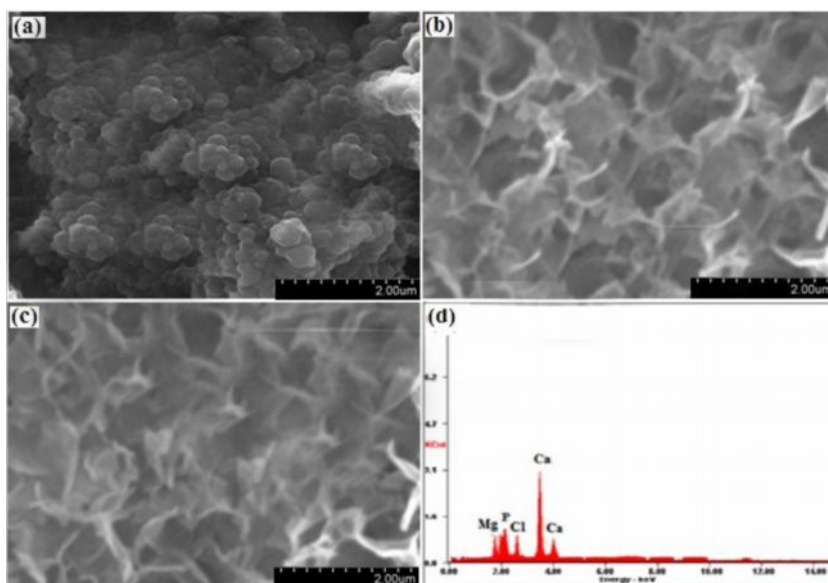


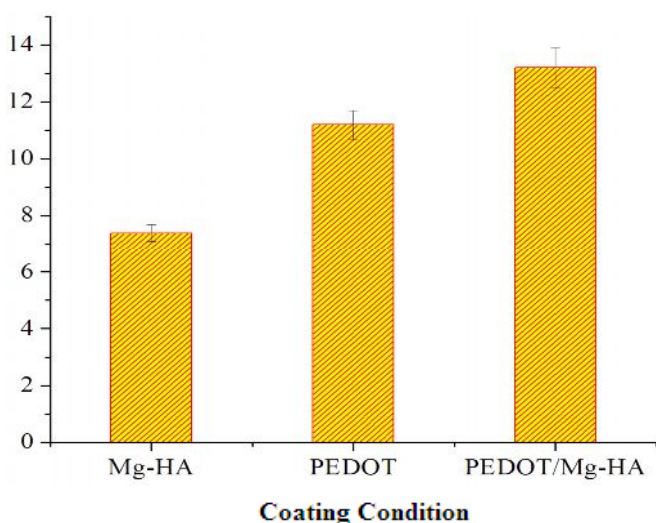
Fig. 3. HRSEM images of (a) PEDOT, (b) Mg-HA, (c) PEDOT/Mg-HA coated 316L SS and (d) EDAX spectrum of PEDOT/Mg-HA bilayer coated 316L SS.

The Fig. 3(c) represents the morphology of PEDOT/Mg-HA bilayer coated 316L SS which exhibits more compact, porous and uniform structure. The porous nature of the Mg-HA coating is a consequence of the  $H_2$  bubbles evolved at the electrode surface. It is attractive to note that most of the interconnected pores which can be favourable for the initiation of bone formation and also can allow the proliferation of diverse cell types responsible for the growth of osseous tissue<sup>14</sup>.

The elemental composition of the PEDOT/Mg-HA bilayer coating on 316L SS is shown in Fig. 3(d). This spectrum indicates the presence of Ca, Mg, C, N, O and P there by confirming the existence of PEDOT/Mg-HA bilayer coatings.

### Adhesion strength

A long-term stability of the 316L SS implant coated with any bioceramic materials and polymers are much more dependent on the adhesion strength of the coating to the 316L SS substrate.



**Fig. 4. Adhesion strength of Mg-HA, PEDOT and PEDOT/Mg-HA coated 316L SS specimens.**

The adhesive strength of the PEDOT/Mg-HA bilayer coating on 316L SS was measured as  $11.2 \pm 0.5$  MPa where as the individual coatings of Mg-HA and PEDOT coated 316L SS exhibited  $7.4 \pm 0.3$  MPa and  $13.2 \pm 0.7$  MPa, respectively. This adhesion strength of the as-coated bilayer sample will make it suitable for orthopaedic applications<sup>14</sup>.

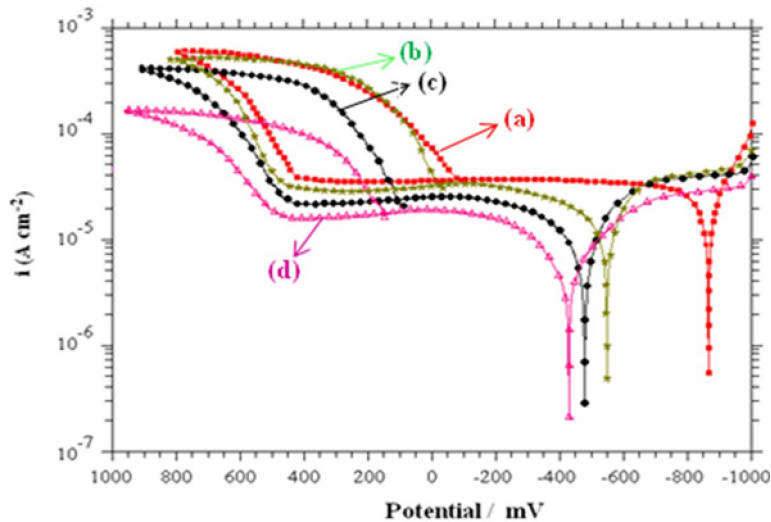
### Electrochemical characterisation

#### Potentiodynamic anodic cyclic polarisation studies

The potentiodynamic polarisation of the uncoated, Mg-HA, PEDOT and PEDOT/Mg-HA bilayer coated 316L SS in Ringer's solution are shown in Fig. 5. The polarisation curves obtained reveal that the corrosion potential ( $E_{corr}$ ), breakdown potential ( $E_b$ ) and repassivation potential ( $E_{pp}$ ) for the uncoated 316L SS were found to be at -870, +449 and -90 mV (vs. SCE), respectively. For the 316L SS samples coated with Mg-HA, the  $E_{corr}$ ,  $E_b$  and  $E_{pp}$  values were found to be -550, +455 and 13 mV vs. SCE, respectively. While the  $E_{corr}$ ,  $E_b$  and  $E_{pp}$  values recorded for the PEDOT coated 316L SS were -475, +621 and +153 mV vs. SCE, respectively.

The polarisation curve obtained for PEDOT/Mg-HA bilayer coated 316L SS, showed  $E_{corr}$ ,  $E_b$  and  $E_{pp}$  values of -435, + 691 and +185 mV vs. SCE., respectively. When compared with the Mg-HA and PEDOT coated 316L SS, the  $E_{corr}$ ,  $E_b$  and  $E_{pp}$  values of the PEDOT/Mg-HA bilayer coated specimens showed better shift towards the nobler direction. In particular, the deposition of bilayer coating showed a significant positive shift than the Mg-HA and PEDOT coating on 316L SS, which implied the enhanced corrosion protective performance in the Ringer's solution. This improved corrosion resistance may arise due to the compact and uniform coating of PEDOT/Mg-HA bilayer on 316L SS samples.





**Fig. 5. Potentiodynamic polarization curves for (a) uncoated, (b) Mg-HA, (c) PEDOT and (d) PEDOT/Mg-HA bilayer coated 316L SS in Ringer's solution.**

## Conclusions

The aim of this study is to enhance the corrosion resistivity and biological activity of 316L SS by developing a bilayer of PEDOT/Mg-HA on it by electrodeposition. The morphological evaluation of the as-formed Mg-HA coating on PEDOT coated 316L SS exhibited an uniform and adherent morphology which indicated that the PEDOT/Mg-HA bilayer coatings could protect 316L SS effectively. The corrosion protection performance of the as-formed bilayer coatings which was evaluated using electrochemical studies revealed that the PEDOT/Mg-HA bilayer coatings significantly improved the corrosion resistance performance of 316L SS sample in Ringer's solution. Hence, the PEDOT/Mg-HA bilayer coated 316L SS will be more effective in orthopedic applications.

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