



# Cathodic protection: A new strategy to enable the formation of nanostructured polypyrrole on magnesium



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## ABSTRACT

Cathodic protection, a conventional technique of protecting metal from corrosion, was used to enable the formation of polypyrrole (PPy) film on biodegradable metal magnesium (Mg). The formation procedure was as follows: first, Mg corrosion was suppressed by applying a negative potential to the Mg cathode; second, oxidant nitrosyl ion ( $\text{NO}^+$ ) was generated on Mg surface through a redox reaction that obtained electron from Mg; third, pyrrole was oxidized to polypyrrole on Mg by  $\text{NO}^+$ . It was interesting to observe that the formed PPy exhibited porous nanostructured morphology. Subsequent corrosion tests showed that the PPy coating could slow down the Mg corrosion in physiological saline, but could not stop corrosion completely, which was especially useful for a coating material of biodegradable metal implants.

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## 1. Introduction

Magnesium (Mg) and its alloys are promising biodegradable metals that have significant potential applications as implants in the field of biomedical science [1,2]. However, their anti-corrosion ability is rather poor [3], which results in their fast degradation within the human body and thus greatly limits their in vivo applications. Therefore, it would be of both scientific and technological interest to slow down the degrade rate of Mg. Using conducting polymers as coating materials may provide an effective way to meet this requirement [4–6]. But unfortunately, although the direct electrochemical deposition of conducting polymers on noble or near noble metals such as gold [7], stainless steel [8] and titanium [9] has been achieved successfully, it is still a challenge to synthesize conducting polymers on active metals, for example, Mg, from aqueous solution due to their high negative electrochemical potential. To date, a few attempts have been made to deposit conducting polymers on Mg, such as coating Mg with noble metal before electrodeposition [10], using ionic liquid [11] or salicylate aqueous solution [12–14] as electrolyte, etc. In these methods, Mg surface was usually passivated by other substances and then used as anode for the electrodeposition of conducting polymers. However, from an electrochemistry point of view, the active metals

that were used as anode are more susceptible to corrosion because the flow of electrons is always from anode to cathode. Recently, Jung et al. reported a new method that allows cathodic deposition of polypyrrole (PPy) on copper [15], in which nitrosyl ion ( $\text{NO}^+$ ), a strong oxidant, was generated only at the copper cathode and therefore the polymerization of pyrrole occurred predominantly on the copper surface. However, their work put main attention on the deposition of PPy on the cathode and did not much emphasize the concept of cathodic protection because the cathode they used, copper, was usually classified as a noble metal.

In this paper, cathodic protection was presented for the first time to protect active metal Mg from corrosion to allow the formation of PPy on its surface. Because Mg corrosion was suppressed by applying a negative potential to the Mg cathode, the oxidation of pyrrole to polypyrrole by  $\text{NO}^+$  on Mg surface was achieved successfully without using any substances as passivator. Furthermore, it was observed that the formed PPy film exhibits porous nanostructured morphology. It is well known that nanostructured conducting polymers have attracted much attention during the past several decades due to their unique properties and promising applications in materials science and nanodevices [16,17]. Currently, the most popular route toward nanostructured conducting polymers is “hard” or “soft” template-assisted method [18]. However, the method is often somewhat tedious and expensive due to the relative complicated synthesis steps or post-treatment process. Therefore, the development of simple and template-free method to prepare conducting polymer nanostructures is still very much

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needed. Here, the method that we proposed to synthesize nanostructured PPy on Mg surface is just such a facile and economical one-step route with no need of any “hard” or “soft” templates. In addition, it should also be pointed out that although PPy nanostructures have been prepared on various metal substrates [19–23], this is the first report on the deposition of such porous PPy nanostructures on Mg. Corrosion tests of the PPy nanostructures were further investigated and it was found that the PPy could reduce the corrosion rate of Mg in physiological saline, but could not stop the corrosion completely. This property was essential for a coating material of biodegradable Mg implant.

## 2. Experimental

### 2.1. Chemicals

Mg (99.99%) was provided by Hui-Ye Magnesium Marketing Co., Ltd (China). Prior to use, Mg foil was abraded with silicon carbide papers (600–2000 mesh), washed and cleaned in ethanol/acetone mixture (1:1) for 10 min in an ultrasonic bath, then dried in a stream of warm air. Pyrrole was purchased from Sinopharm Chemical Reagent Co., Ltd (China), distilled under the protection of nitrogen gas and stored frozen. All other chemicals were of analytical grade and used as received. Milli-Q water from a Millipore Q water purification system was used throughout.

### 2.2. Deposition of PPy on Mg and Fe

The preparation of porous PPy nanostructures on Mg and Fe was carried out at room temperature in a one-compartment cell by the use of CHI660D Electrochemical Workstation (Chenhua Instrument Co., Ltd., China), where the Mg and Fe foil with active area of  $1\text{ cm} \times 1\text{ cm}$  was used as the cathode and a platinum wire served as the counter electrode. All potentials were referred to a saturated calomel electrode (SCE). The porous nanostructure of PPy was synthesized on the Mg foil in an electrolyte containing 0.20 M pyrrole, 0.50 M  $\text{NaNO}_3$  and 0.35 M  $\text{HNO}_3$  under a constant potential for 1800 s. Prior to each polymerization step, the electrolyte solution was degassed with a nitrogen flow for 5 min. After the polymerization, the Mg foil with the porous nanostructure of PPy on its surface was removed from the electrolyte and rinsed thoroughly with de-ionized water, and then dried in air at room temperature. The synthesis procedure for the porous nanostructure of PPy on Fe foil was the same as that described above, except that the Mg foil was replaced by Fe foil.

### 2.3. Characterization and measurement

The surface morphologies of the PPy were examined by a scanning electron microscope (SEM, LEO1530, Germany) operated at 20 kV. Fourier transform infrared (FTIR) spectroscopy was recorded on an Avatar 360 spectrophotometer (Thermo Nicolet, USA). The linear polarization measurements (Tafel) were performed in 0.9 wt% NaCl solution in a range of  $\pm 250\text{ mV}$  using the CHI660D Electrochemical Workstation at  $25^\circ\text{C}$  (scan rate =  $1\text{ mV/s}$ ). The electrochemical impedance spectrum (EIS) was carried out in 0.9 wt% NaCl solution at  $25^\circ\text{C}$  with a CHI660D Electrochemical Workstation using 5 mV (rms) AC sinusoid signal at a frequency range from 1000 kHz to 0.1 Hz.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 400 MHz solid-state NMR spectrometer.

## 3. Results and discussion

Fig. 1a showed a digital photo of the PPy film. It was observed that the exposed active area of the Mg foil was covered completely

by a black PPy film that looked quite uniform and compact. Fig. 1b displayed the SEM image of the surface microstructure of the PPy film synthesized at the potential of  $-2.2\text{ V}$  for 1800 s. It could be seen clearly that the PPy film exhibited fine porous nanostructure with homogeneous pores, which was totally different from the nanoparticle morphology of the PPy formed on copper [15]. The thickness of the backbone of the porous nanostructure was about 90 nm. Fig. 1c revealed the FTIR spectrum of the PPy film. The existence of the characteristic PPy peaks, such as the asymmetric and symmetric ring stretching at 1569 and  $1463\text{ cm}^{-1}$ , the C–N stretching vibration at  $1194\text{ cm}^{-1}$ , and C–H wagging vibrations at  $781\text{ cm}^{-1}$ , indicated the formation of PPy [24,25]. Moreover, the solid state  $^{13}\text{C}$  NMR of the porous PPy nanostructure was also performed. As Fig. 1d showed, there were three  $^{13}\text{C}$  peaks at ca. 124, 127, and 133 ppm. The first and third peaks corresponded to  $\beta$ - and  $\alpha$ -carbon, respectively. The second peak was induced by nitrogen atom [26]. Therefore, the  $^{13}\text{C}$  NMR result also confirmed the presence of PPy.

We suggest three factors influence the structure of the porous PPy and the conditions used for its preparation.

First, the application of the negative potential provided a cathodic protection for the Mg foil and thus the tendency of losing electron from Mg was suppressed. According to the Pourbaix diagram [27,28], the corrosion potential of Mg is about  $-2.37\text{ V}$  under acidic conditions at  $25^\circ\text{C}$ . Therefore the negative potentials around  $-2.37\text{ V}$  were used to protect the Mg foil from corrosion in the present work. It was found that the similar porous nanostructure of PPy could be formed on the Mg foil within the potential range from  $-1.90$  to  $-2.80\text{ V}$ . However, although the porous nanostructure of PPy could be prepared at  $-1.90\text{ V}$ , its morphology showed a more irregular structure and the thickness of the backbone was thicker and shorter than others due to the relatively serious Mg corrosion (Fig. 2a). The deposition potentials less negative than  $-1.90\text{ V}$  would cause very severe Mg corrosion, which prevented the adherence of the PPy on Mg foil. As the potential was made more negative than  $-1.90\text{ V}$ , more uniform porous nanostructure was formed. However, the amount of the hydrogen bubbles that generated from the Mg foil increased as the potential was made more negative. As a result, non-uniform porous nanostructure of PPy with big and small holes coexisted was obtained as the potential was made to  $-2.80\text{ V}$  (Fig. 2b). As expected, excessive hydrogen bubbles would be generated when the potential was made more negative than  $-2.80\text{ V}$ , which significantly hindered the polymerization of pyrrole on Mg surface and thus no continuous PPy film formed. In addition, the experiment without applying the negative potential on Mg was performed for comparison. The severe Mg corrosion was observed and the PPy film could not be formed on its surface. This result indicated that the application of the negative potential was a prerequisite for the formation of PPy coating on Mg. Furthermore, the effect of PPy morphology on the PPy conductivity was investigated. The conductivities of the porous nanostructures of PPy synthesized at  $-1.9$ ,  $-2.2$ , and  $-2.8\text{ V}$  were measured by the four-probe technique at room temperature and the values were  $2.5 \times 10^{-2}$ ,  $8.2 \times 10^{-2}$ , and  $1.3 \times 10^{-1}\text{ S cm}^{-1}$ , respectively. These values were comparable to those of the PPy nanostructures with similar morphologies [29,30]. It was found that the conductivity was increased with the decreasing of the porous PPy backbone thicknesses. This may be because decreasing backbone thickness increases the number density of the branches of the porous nanostructures, thus leading to improved connectivity and conductivity.

Second, the oxidant,  $\text{NO}^+$  ion, was generated on Mg surface and responsible for the oxidation of pyrrole. As described in Section 2, the electrolyte solution was composed of pyrrole (0.20 M),  $\text{NaNO}_3$  (0.50 M) and  $\text{HNO}_3$  (0.35 M). The pH of the electrolyte was 0.5. The formation process of the  $\text{NO}^+$  should be as follows [15]. Firstly,

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