

## Effect of Post Heat Treatment on Corrosion Resistance of Phytic Acid Conversion Coated Magnesium

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An environment friendly chemical conversion coating for magnesium was obtained by using a phytic acid solution. The effect of post-coating 1 heat treatment on the microstructures and corrosion properties of phytic acid conversion coated magnesium was investigated. It was observed that the microstructure and corrosion resistive properties were improved for the heat treated samples. The corrosion current density for bare magnesium, phytic acid conversion coated magnesium, and post-coating heat treated magnesium was calculated to be  $2.48 \times 10^{-5}$ ,  $1.18 \times 10^{-6}$ , and  $9.27 \times 10^{-7}$  A/cm<sup>2</sup>, respectively. The lowest corrosion current density for the heat treated sample indicated its highest corrosion resistive effect for the magnesium. The maximum corrosion protective nature of the heat treated sample was further confirmed by the largest value of impedance in electrochemical impedance spectroscopy studies.

**KEY WORDS:** Magnesium; Phytic acid; Corrosion; Impedance spectroscopy; Scanning electron microscopy

### 1. Introduction

Magnesium and its selected alloys have several advantageous properties such as light weight, natural abundance, and castability<sup>[1]</sup>. To add further importance, magnesium has lately been demonstrated to be biocompatible as well as biodegradable<sup>[2]</sup>. Due to these unique properties, magnesium and its alloys have been used in various applications that include biomedical, automobile, and aeronautical applications<sup>[3–5]</sup>. However, one of the major drawbacks that hinder the extensive applications of magnesium is its high corrosion rate<sup>[6]</sup>. Magnesium degrades quickly in humid, saline, and body fluids environments<sup>[7]</sup>. Alloying with other elements<sup>[8]</sup>, making composites<sup>[9]</sup> and surface treatments<sup>[10]</sup> are some of the ways to improve the corrosion resistance of the magnesium. Among the surface modification techniques, chromate conversion coating is a very common and effective conversion coating<sup>[11,12]</sup>. But the toxic nature of the hexavalent chromium ion and its adverse effect on environment have led researchers to explore and develop non-toxic and environment friendly surface treatment methods for improving the corrosion resistance of magnesium and its alloys<sup>[13]</sup>.

Recently, phytic acid has been used as a green conversion coating for magnesium and its alloys<sup>[14,15]</sup>. Phytic acid (C<sub>6</sub>H<sub>18</sub>O<sub>24</sub>P<sub>6</sub>) is an organic macromolecule consisting of 24 oxygen atoms, 12 hydroxyl groups, and 6 phosphate carboxyl groups. Phytic acid is a naturally occurring material that is non-toxic, biocompatible, and green to the environment. It is mostly found in legume seed, cereal grains, nuts, and beans<sup>[14,16,17]</sup>. The active groups of phytic acid can react with metal ions such as magnesium, and form stable chelate compounds on the surface of magnesium which can slow down the corrosion of magnesium<sup>[18,19]</sup>. Liu et al.<sup>[18]</sup> have systematically studied the corrosion resistive property of phytic acid coated magnesium alloy as a function of immersion time, temperature, pH value, and concentration of phytic acid. According to them, the corrosion resistive properties of phytic acid conversion coated magnesium alloy were comparable with that of chromate conversion coated magnesium alloy. However, the presence of micro-cracks in phytic acid conversion coated samples impairs its corrosion resistive effect<sup>[20]</sup>. It is in this context that we have addressed the issue of micro-cracks and offered a simple experimental solution based on post-coating heat treatment. To the best of our knowledge, the effect of a post-coating heat treatment of phytic acid conversion coated magnesium on the microstructure and its resulting corrosion property has not been reported. We have observed that a post-coating heat treatment procedure annihilates the micro-cracks in the phytic acid conversion coated layer that in turn reduces the percolation and permeation of reactive ions in the solution to magnesium substrate. This effectively results in the increase of the corrosion resistance of magnesium substrates.

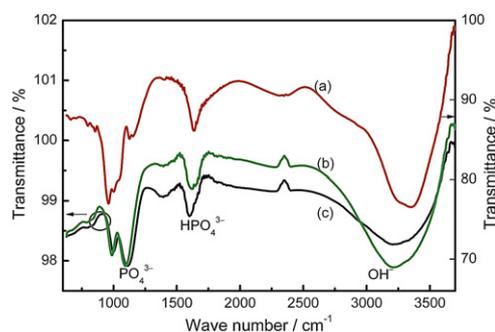
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## 2. Experimental

High purity (99.9%, GoodFellow, Germany) magnesium substrates were used for this study. The magnesium substrates for the conversion coating were prepared by cutting magnesium rod (25.4 mm diameter) with a thickness of  $\sim 1.1$  mm. Before the conversion coating, the magnesium substrate was progressively polished with SiC paper up to grade 1200#, followed by degreasing with acetone. The phytic acid conversion coatings were formed by dipping the magnesium in the phytic acid solution (50 wt% H<sub>2</sub>O) at room temperature for 3 h. The immersion time has been optimized to get the lowest corrosion current density. After immersion, the coated substrates were washed using deionized water and dried at room temperature. The heat treatment of phytic acid conversion coated magnesium was carried out by heating at 95 °C for 1 h under vacuum. Hereafter, sample 1, sample 2, and sample 3 represents bare magnesium, phytic acid conversion coated magnesium, and post-coating heat treated phytic acid conversion coated magnesium, respectively. Schematic diagram of the coating process and the effect of post-coating heat treatment is shown in Fig. 1(a).

Effect of heat treatment on the chemical nature of the coatings was studied using a Fourier transform infrared spectrophotometer (Agilent/Varian 670 Mid-Near FT-IR Spectrometer). The Infrared (IR) spectra were recorded in attenuated total reflectance (ATR) mode. The structural characterizations of the samples were performed by X-ray diffraction (XRD) technique. The XRD spectra of the films were recorded with Bruker AXS (D8 Discover) X-ray diffractometer using the  $2\theta$ – $\theta$  scan with CuK $\alpha$  ( $\lambda = 0.15405$  nm) radiation. The microstructures of the bare and coated magnesium samples were recorded before and after corrosion process using a scanning electron microscope (SU8000, Hitachi). The energy dispersive X-ray spectrometer (Quantax 200, Bruker) was used to examine the elemental compositions of the coatings.

DC potentiodynamic polarization measurements were performed in  $1\times$  phosphate buffered saline (PBS) solution using

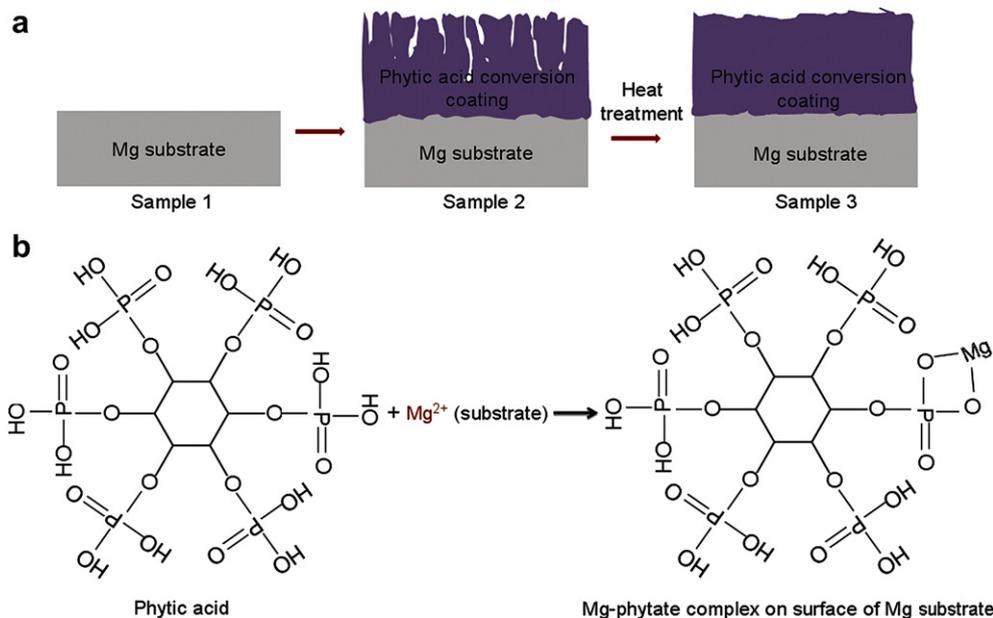


**Fig. 2** FT-IR spectra of as-received phytic acid (a), and phytic acid conversion coated magnesium substrates before (b) and after (c) heat treatment.

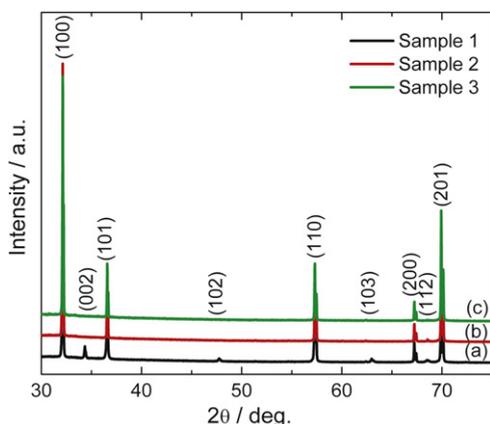
Gamry potentiostat (R600, Gamry Instruments) with a standard three-electrode configuration. A Ag/AgCl (saturated KCl) electrode and platinum wire were used as the reference and counter electrodes, respectively. Bare and coated magnesium were used as the working electrode. All the measurements were carried out at room temperature. The polarization measurements were carried out in the applied potential range of  $\pm 300$  mV vs SCE, at 5 mV/s scan rate. Corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $I_{\text{corr}}$ ) were determined using the Echem analyst software (Gamry Instruments). The electrochemical impedance spectroscopy (EIS) study was performed in the frequency range of 0.1– $10^6$  Hz under 10 mV amplitude of the perturbation signal.

## 3. Results and Discussion

The mechanism of the phytic acid conversion coating on magnesium is shown in Fig. 1(b). As seen in Fig. 1(b), the hydroxyl group of phytic acid can react with the magnesium ions to form a conversion coating on the surface of magnesium. In aqueous solution, the phosphate group of the phytic acid ionizes



**Fig. 1** (a) Schematic diagram of the conversion coating process, (b) proposed mechanism of the phytic acid conversion coating on magnesium substrate.



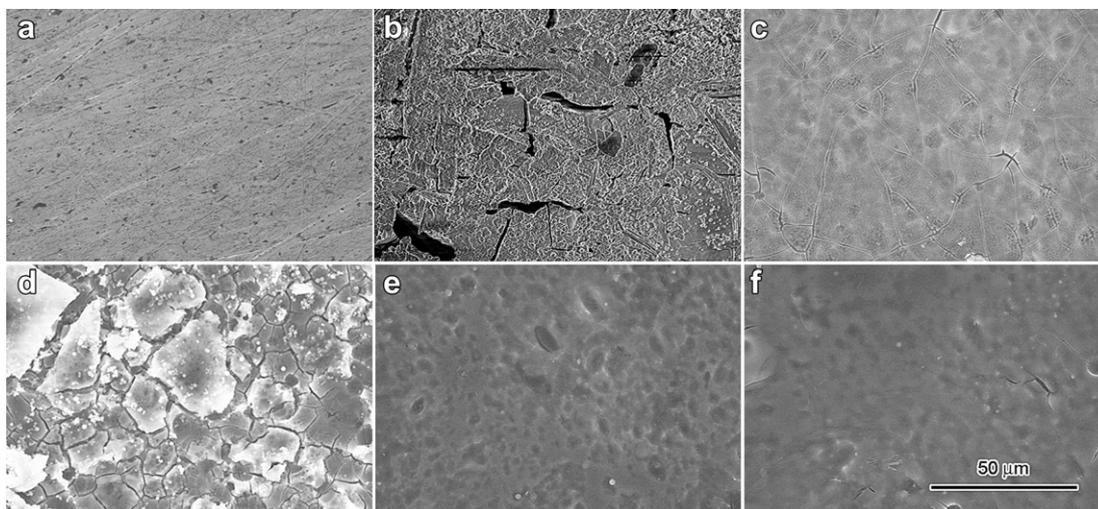
**Fig. 3** XRD patterns of bare magnesium (sample 1) (a), phytic acid conversion coated magnesium (sample 2) (b), and post-coating heat treated phytic acid conversion coated magnesium (sample 3) (c).

to form phytic acid radical with different number of phosphate radical, phosphate hydrogen radical, and hydroxyl ions. At the same time, a large number of magnesium ions are produced at the initial stage when the magnesium is immersed in the phytic acid solution. These surface magnesium ions combine with phytic acid ion to form magnesium phytate complex on the surface of the magnesium substrate<sup>[13]</sup>.

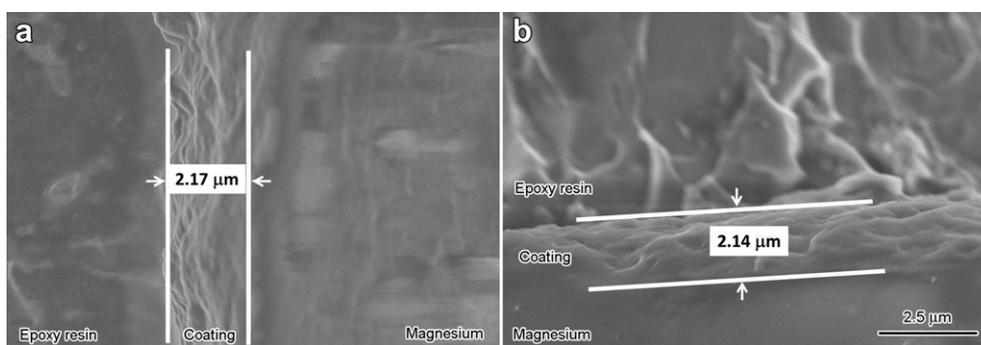
The Fourier transform infrared (FT-IR) spectra recorded from as-received phytic acid and phytic acid conversion coated magnesium substrates before and after the heat treatment are shown in Fig. 2. As seen in Fig. 2, the characteristic bands of phytic acid were observed for  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{3-}$  and  $\text{OH}^-$ <sup>[13]</sup>. All the characteristic bands for the as-received phytic acid were also observed in the phytic acid conversion coated magnesium samples. This figure also shows that there is no change in the characteristic band positions for  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{3-}$  and  $\text{OH}^-$  in the heat treated sample. This could be taken to indicate that the chemical nature of the conversion coating is not affected by the post heat treatment process.

The effect of heat treatment on the structural property of phytic acid conversion coated magnesium was analyzed by XRD measurements. The XRD patterns of all the samples are shown in Fig. 3. As seen in this figure, all the samples show multiple peaks and are polycrystalline in nature. All the peaks arising from magnesium substrate were found to be in good agreement with the hexagonal phase of magnesium (JCPDS file No. 035-0821). Similarly, no other peaks besides the peaks corresponding to magnesium substrate were observed in the phytic acid conversion coated samples even after the heat treatment. The absence of any peaks other than those arising from pure magnesium suggests that there is no oxide formation on the substrate surface during the heat treatment of the samples.

The effect of phytic acid conversion coating and the post-coating heat treatment on the microstructure of magnesium was studied by scanning electron microscopy (SEM). Fig. 4 shows the micro-images of sample 1, sample 2, and sample 3. These images were taken before and after the corrosion study. It is observed that the microstructure of the phytic acid coated magnesium is improved after heat treatment. As seen in Fig. 4, phytic acid coated magnesium (sample 2) shows some micro-cracks whereas heat treated sample (sample 3) is free from such micro-cracks. The presence of the micro-cracks in the sample 2 can lead to pitting and crevice corrosion. However the heat treated samples prevent the transport of electrons and ions from solution to magnesium surface and thus reduces the corrosion of magnesium. The thicknesses of the coating were measured using a cross-section scanning electron microscope. The thickness of the samples before and after heat treatment was measured by cross-section SEM as shown in Fig. 5. A comparison of the thickness of samples before and after heat treatment indicates a very slight shrinkage ( $\sim 1.4\%$ ) in the film thickness due to the heat treatment. The thickness of sample 2 and sample 3 was measured to be 2.17 and 2.14  $\mu\text{m}$ , respectively. The chemical composition of the coating before and after the heat treatment was analyzed by EDS and the results are shown in Fig. 6. As seen in the EDS spectra, there is no difference in the phytic acid coated magnesium before and after heat treatment. It is noted that the coating is mainly composed of Mg, O, P, and C elements. The presence of P indicates



**Fig. 4** SEM images of the bare magnesium (sample 1) before (a) and after (b) corrosion, phytic acid conversion coated magnesium (sample 2) before (c) and after (d) corrosion, and post-coating heat treated phytic acid conversion coated magnesium (sample 3) before (e) and after (f) corrosion.



**Fig. 5** SEM images of cross-section of phytic acid conversion coated magnesium (sample 2) (a), and post-coating heat treated phytic acid conversion coated magnesium (sample 3) (b).

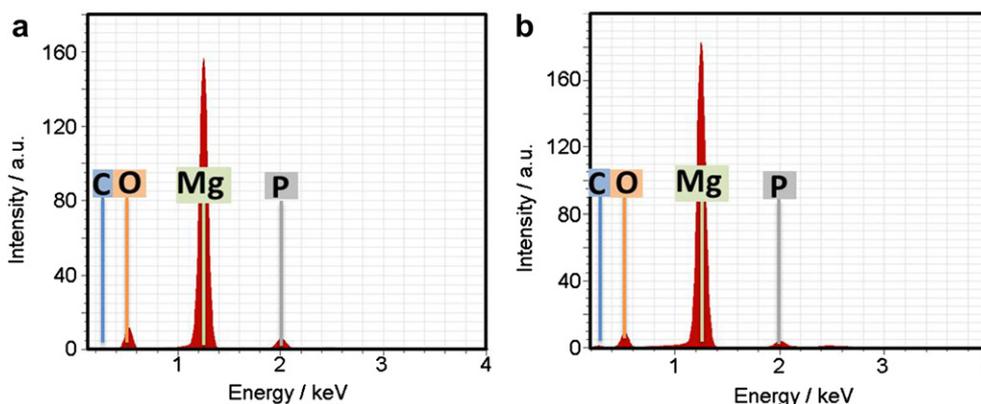
a realization of a successful conversion coating of magnesium with phytic acid<sup>[21]</sup>.

The adhesion test of any coating on the substrate is a very important factor to determine the quality of the coating for its proper applications. Low quality films could peel off from the substrate and hence are of little importance toward their beneficial application for substrate. The adhesion strength of the conversion coating on the magnesium was performed according to the standard of American Society for Testing Materials (ASTM)<sup>[22]</sup>. An ASTM-D3359-02 tape test was performed to see the adhesion of phytic acid conversion coatings on magnesium substrate using cross cut patterns through the coating. The results obtained using the tape test are shown in Fig. 7. As seen in these optical images, the entire coating remains intact after peeling off the tape stuck to the samples. These results suggest that the coatings have strong adhesion to the magnesium substrate.

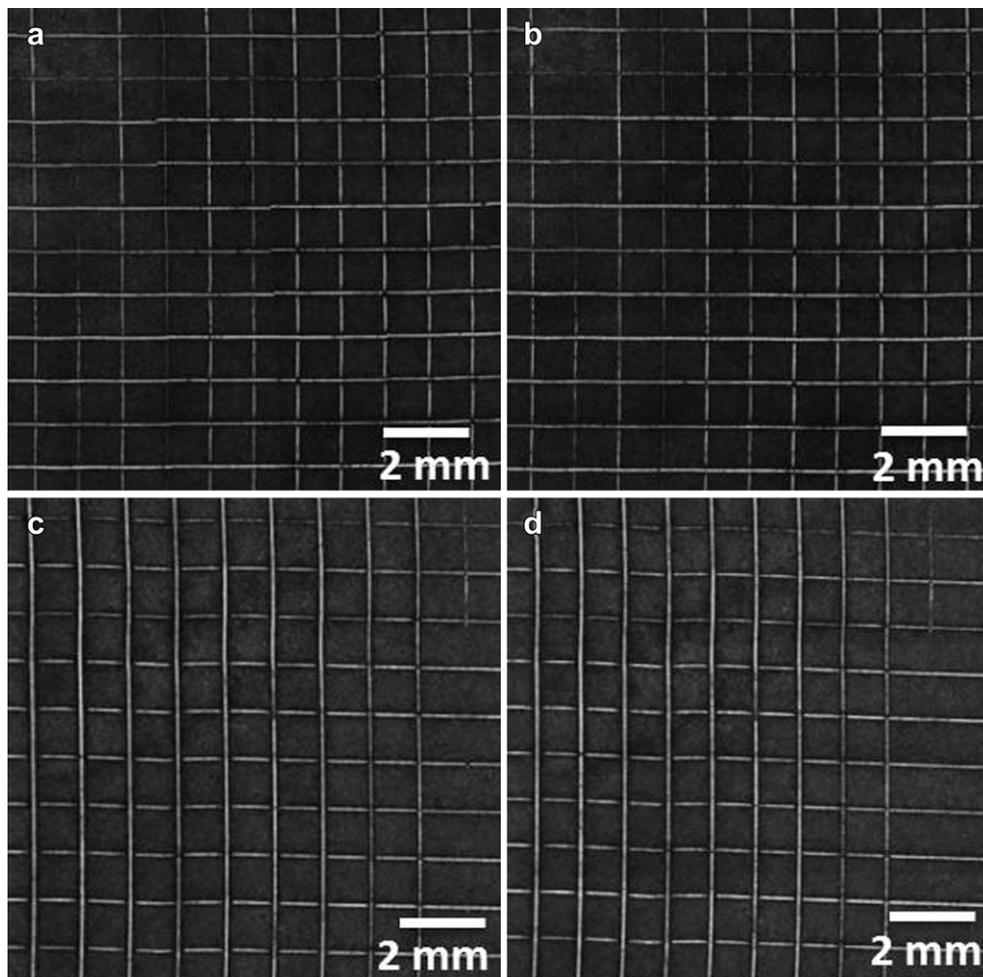
The degradation of all the samples was studied using the volume of hydrogen gas released by immersing the samples in the PBS solution at 37 °C in a water bath. Hydrogen gas released due to the corrosion of magnesium was collected into a burette and the reading of total volume of hydrogen gas evolved was recorded at a regular time interval. Fig. 8 shows the volume of hydrogen gas evolved as a function of immersion time for different samples. As seen in Fig. 8, the volume of hydrogen gas evolved for bare magnesium is higher than that of phytic acid conversion coated magnesium samples. In the hydrogen release test, it was observed that the heat treated sample (sample 3) shows reduced hydrogen

releases which could be due to the formation of microstructures free from cracks. The surface free from micro-cracks is expected to reduce the penetration of reactive ions from PBS solution to magnesium substrate and thereby reducing the corrosion of magnesium. Monitoring of the pH of the solutions with samples immersed in them suggests that solutions pH is almost constant ( $\sim 7.3$ ) during the measurements.

The effect of phytic acid conversion coating and post-coating heat treatment on the corrosion property of magnesium was studied by potentiodynamic polarization and electrochemical impedance measurements. Before potentiodynamic polarization measurements, the steady state reaction condition was achieved by immersing the samples in the PBS solution for 15 min. The steady state corrosion reaction condition was verified by monitoring open-circuit potential. Fig. 9 shows the potentiodynamic polarization curves for the three types of samples as designated in Fig. 1. It is clear from this figure that sample 2 and sample 3 have superior corrosion potential compared to sample 1. As seen in Fig. 9, the corrosion current density of the sample 2 and sample 3 is also lower than that of sample 1. The corrosion potentials, estimated from the linear parts of the Tafel plots<sup>[23]</sup> for sample 1, sample 2, and sample 3 were found to be  $-1.64$ ,  $-1.50$  and  $-1.58$  V, respectively. Whereas, the corrosion current densities for sample 1, sample 2, and sample 3 were calculated to be  $2.48 \times 10^{-5}$ ,  $1.18 \times 10^{-6}$  and  $9.27 \times 10^{-7}$  A/cm<sup>2</sup>, respectively. The lowest current density observed for sample 3 indicates that the heat treated sample is the most corrosion resistive in nature<sup>[24]</sup>.



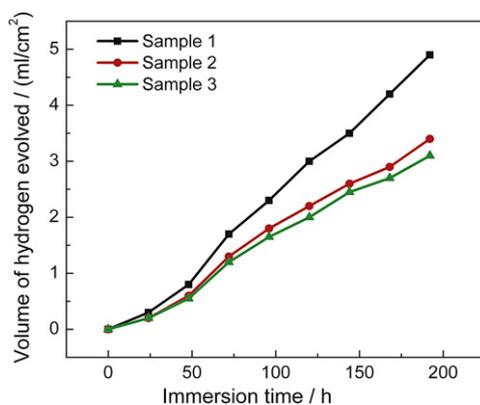
**Fig. 6** EDS spectra of phytic acid conversion coated magnesium (sample 2) (a), and post-coating heat treated phytic acid conversion coated magnesium (sample 3) (b).



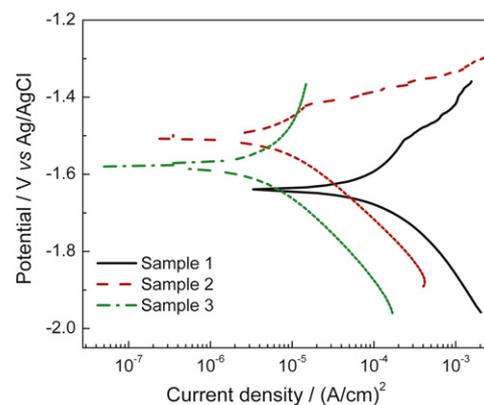
**Fig. 7** Optical images of phytic acid conversion coated magnesium (sample 2) before (a) and after (b) adhesion test, and post-coating heat treated phytic acid conversion coated magnesium (sample 3) before (c) and after (d) adhesion test.

The electrochemical impedance spectroscopy (EIS) technique has been used to study the degradation processes of the bare and coated materials<sup>[25,26]</sup>. The EIS technique allows the corrosion of a coating to be evaluated from the changes induced in impedance

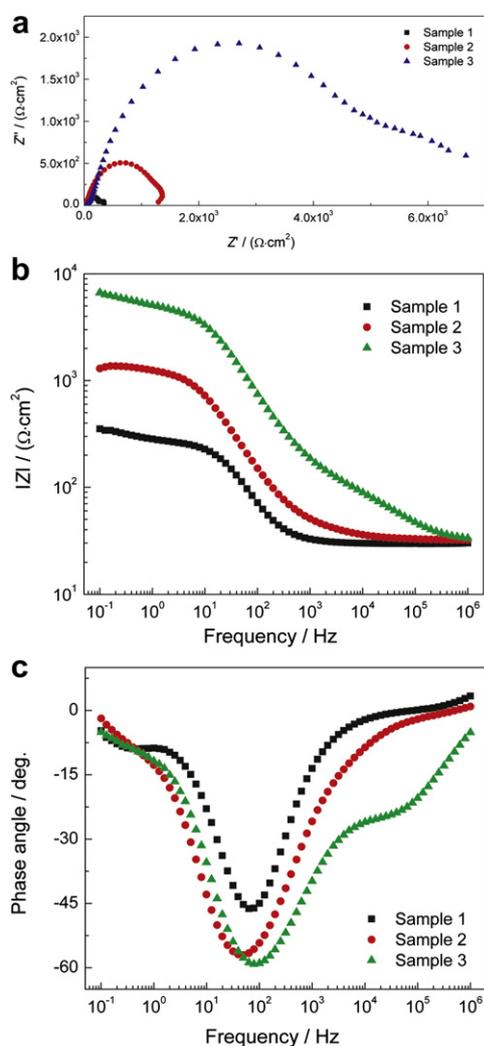
diagrams. The EIS measurements were recorded at the open-circuit potential after stabilizing in PBS solution for 15 min. Fig. 10 shows the Nyquist and Bode plots for the uncoated and coated magnesium substrates. As seen in the Nyquist plot (Fig. 10(a)), the real part of the impedance ( $Z'$ ) for the sample 3



**Fig. 8** Volume of hydrogen gas released versus time plots for bare magnesium (sample 1), phytic acid conversion coated magnesium (sample 2), and post-coating heat treated phytic acid conversion coated magnesium (sample 3) samples in  $1 \times$  PBS solution.



**Fig. 9** Potentiodynamic polarization curves for bare magnesium (sample 1), phytic acid conversion coated magnesium (sample 2), and post-coating heat treated phytic acid conversion coated magnesium (sample 3).



**Fig. 10** Nyquist plot (a),  $|Z|$  vs  $\log f$  (b), and phase angle vs  $\log f$  plots (Bode plots) (c) for bare magnesium (sample 1), phytic acid conversion coated magnesium (sample 2), and post-coating heat treated phytic acid conversion coated magnesium (sample 3).

is the highest among other samples, indicating the highest degree of corrosion protection for the magnesium. The maximum corrosion protective nature of the sample 3 was further confirmed by the largest value of  $|Z|$  in the Bode plot (Fig. 10(b))<sup>[27]</sup>. In the Bode diagram for the phase (Fig. 10(c)), a greater flattening of the maximum for the sample 3 implies a greater compactness of the coating on the magnesium<sup>[28]</sup>. Some important parameters such as impedance, resistance, and phase angle were estimated from the EIS data for different samples and tabulated for easy comparison (Table 1). As evident from this table, the heat treated sample (sample 3) has the largest

**Table 1** Some electronic parameters obtained from EIS measurements

	Phase angle, $\theta$ (deg.) at 10 kHz	$\log Z $ ( $\Omega \text{ cm}^2$ ) at 100 mHz	$R_{\text{total}}$ ( $\Omega \text{ cm}^2$ )
Sample 1	2.17	352	329
Sample 2	8.61	1297	1121
Sample 3	26.03	6688	6513

impedance and total resistance (excluding the solution resistance). The highest resistance of the sample 3 would provide the greatest barrier for the penetration of active  $\text{Cl}^-$  and water, subsequently enhancing the corrosion resistance to magnesium<sup>[29]</sup>. The compactness of the coating was compared based on the phase angle. The phase angle has been used to study the compactness of the coatings and their corrosion resistive properties<sup>[30]</sup>. The lowest and the highest intactness were observed at phase angle near to 0 and  $90^\circ$ , respectively. So the increase in the phase angle shows the increase in coating intactness<sup>[31]</sup>. As seen in Table 1, sample 3 shows the highest phase angle, indicating the highest compactness compared to other samples.

#### 4. Conclusion

An environmental friendly conversion coating on magnesium was developed using phytic acid. The microstructure and corrosion resistive properties of phytic acid conversion coated magnesium were further improved after the heat treatment. The corrosion current density for phytic acid conversion coated, and heat treated samples was found to be lower than that of bare magnesium substrates. The highest value of impedance for the heat treated sample confirmed that the heat treatment after phytic acid coating improved its corrosion resistive properties.

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