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Complete List of Authors:	Deyab, M; Egyptian petroleum research institute, , Analysis and Evaluation Dep. Ouarsal, Rachid ; Université Sidi Mohamed Ben Abdellah Al-Sabagh, A ; Egyptian Petroleum Research Institute Lachkar, Mohammed ; Université Sidi Mohamed Ben Abdellah El Bali, B. ; Université Sidi Mohamed Ben Abdellah

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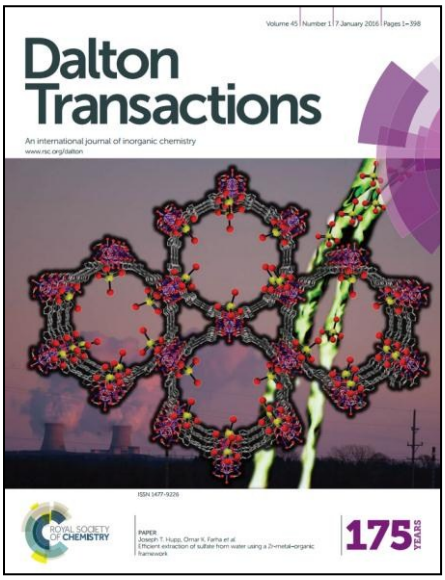

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Anticorrosive coating is highly important, because corrosion reduces the strength of structural materials and this destruction involves direct and indirect losses including problems related to human safety and facts concerning natural resources conservation.

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Inorganic compounds are an integral part of anticorrosion paints. At present, close attention is paid especially to the research and development of non-toxic anticorrosive materials that can replace pigments based on lead and chromium.

The synthesis of transition metal phosphates compounds with open-framework structures has been extensively studied due to their applications in adsorption, catalysis, electronics, ionic conduction, ion-exchange processes, magnetism and separation.

In this work, studies have been made in order to introduce new generation of epoxy coatings mostly based on new hydrogenphosphate compounds $(NH_4)_2[Mg(H_2O)_6]_3(HPO_3)_4$.

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Enhancement of corrosion protection performance of epoxy coating by introducing new hydrogenphosphate compound

M. A. Deyab[1*], Rachid Ouarsal[2], A. M. Al-Sabagh[1] , Mohammed Lachkar[2], B. El Bali[2]

[1]Egyptian Petroleum Research Institute (EPRI), PO Box 11727, Nasr City, Cairo, Egypt

[2]Laboratoire d'Ingénierie des Matériaux Organométalliques et Moléculaires, Unité Associée au CNRST (URAC 19), Faculté des Sciences, Université Sidi Mohamed Ben Abdellah, B.P.1796 (Atlas), 30000 Fès, Morocco.

* Corresponding author. Tel.: +201006137150; fax: + 202 22747433 E-mail address: hamadadeiab@yahoo.com

Abstract

$(NH_4)_2[Mg(H_2O)_6]_3(HPO_3)_4$ (MgHP) was synthesized by a wet chemistry route and characterized by IR spectroscopy. The influence of MgHP on the anti-corrosion and mechanical properties of epoxy coating were investigated using electrochemical impedance spectroscopy (EIS), nano-indentation and scanning electron microscopy (SEM) techniques as well as the water uptake measurements. Results showed that the incorporation of MgHP particles increased anti-corrosion and mechanical properties of epoxy coating. The epoxy coating performance enhances with increasing

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concentration of MgHP particles up 1.0%. It was observed that the volume of water uptake by epoxy coating reduced after modification with MgHP particles as compared to neat epoxy coating.

Keyword: epoxy coating; Corrosion resistance; hydrogenphosphate; electrochemical; carbon steel

1. Introduction

The synthesis of transition metal phosphates compounds with open-framework structures has been extensively studied due to their applications in adsorption, catalysis, electronics, ionic conduction, ion-exchange processes, magnetism and separation [1-5].

Replacement of [PO_4]-phosphate by [HPO_3/H_2PO_3]-phosphite groups allowed the preparation of a new class of metal phosphite compounds, where phosphorus at its low oxidation state (+3), with original structural frameworks, varying from 0-D cluster to 3-D open-framework structures are obtained [6-13]. Generally, a transition metal phosphite is synthesized mainly by a direct reaction between H_3PO_3 and the metals ions [14, 15].

However, few simple phosphite compounds containing either Mg^{+2}, and mixed contain also an alkali/ammonium cations are known: $MgHPO_3(H_2O)_6$ [16], $NaMg(H_2PO_3)_3.(H_2O)$[17] and the title compound $(NH_4)_2[Mg(H_2O)_6]_3(HPO_3)_4$ which have been twice reported [18, 19].

Carbon steel has been widely employed as construction materials for pipe work in the oil and gas production [20-21].

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The efficiency of cathodic protection (CP) method on carbon steel pipelines can be improved by organic coatings [22-23].

Barrier coatings can be used alone or in combination with impressed current driven cathodic protection systems, where they act to minimize exposed cathode areas and thereby reduce the cost of required electricity that maintains the direction of current flow [24]

Increasing cathodic protection is often considered as the best or only solution to prevent corrosion on a pipeline with poor or disbonded coatings [25]. The CP may help to protect pipelines exposed to the electrolyte, but it does not always protect the pipe under many types of disbonded coatings, therefore corrosion will continue unless these coatings are replaced [26].

Organic coatings can protect metal substrates from corrosion via two mechanisms. The first one is the electrochemical mechanism where it inhibits the corrosive reactions by sharing an anticorrosive pigment in the passivation of the metal, forming stable and strongly adhesive layers on the substrate. The second mechanism is the barrier mechanism. Where it depends on the inhibiting the access of corrosive environmental agents to the metal surface [27-29].

Organic coating film has limited lifetime and finally decays, allowing corrosive ions to contact with the substrate. The barrier performance of coatings can be enhanced by the incorporation of inorganic filler particles

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[29-33]. This particles increase the coating performance by decreasing the porosity and zigzagging the diffusion path for deleterious species [34].

Chromate based pigments provide high corrosion resistance. However, because of the environmental rules, more demands are being made for alternative inorganic filler particles [35].

In this work, studies have been made in order to introduce new generation of epoxy coatings mostly based on new hydrogenphosphate compounds $(NH_4)_2[Mg(H_2O)_6]_3(HPO_3)_4$.

In fact, the the hydrogenophosphates represent a family of compounds with great potential for the generation of new proton conductors. A great deal of theoretical and experimental work has been devoted to protonic conductors [36,37], due to their potential as electrolyte for the production of electricity in hydrogen fuel cells.

The present study is a continuation of our contribution in the application of phosphates as anti-corrosive compounds [38-41].

We hereby evaluate the effect the effect MgHP on the mechanical and anti-corrosion performance of epoxy-coated carbon steel during immersion in 3.5% NaCl solution using electrochemical techniques and morphology analysis.

2. Experimental

2.1. Synthesis of $(NH_4)_2[Mg(H_2O)_6]_3(HPO_3)_4$

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1.0 g of magnesium oxide (MgO) was added to a solution of 4.0 g phosphorous acide H_3PO_3 dissolved in 15 mL water (S1), which was stirred for 1 h at 333 K. An equimolar preparation of another solution (S2), containing $(NH_4)_2HPO_3$, was added. The two solutions S1 and S2 were mixed and stirred for 1 h at room temperature, after which the obtained precipitate was filtered out. The filtrate was allowed to stand at room temperature. After 2 weeks, colorless crystals are obtained; they were washed with an ethanol-water (80–20%).

2.2. Preparation of coating and coated samples

The coating formula was made by mixing epoxy resin (Bisphenol – from Ciba Co.), polyamidoamine hardener (CRAYAMID- from Arkema Co.) and different concentrations (from 0.2% to 1.0%) of MgHP. The weight ratio of the epoxy resin to the hardener was 2:1. All the contents were mixed using a speed mixer (H500 homogenizer form POL-EKO-APARATURA) for 30 min.

Carbon steel sheets (industrial grade) were used as the substrates. The test sheets (15 mm × 20 mm × 0.70 mm) were pretreated by mechanical cleaning, degreasing in an acetone solution and rinsing with distilled water.

The clean carbon steel substrate was dipped into the finally coating formula for one time and then kept in an oven at 393 K for 1.0 h to allow full curing. Dry film thickness for all samples was 80 ± 10 μm.

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2.3. Test of the corrosion protection performance

For investigation of the corrosion protection performance of coating systems, the electrochemical impedance spectroscopy (EIS) measurements were measured using EG-G 273 potentiostat/ galvanostat. A three electrode cell design was used for electrochemical experiments. The cell was constructed with platinum as an auxiliary electrode, coated carbon steel as a working electrode and saturated calomel electrode (SCE) as a reference electrode.

Impedance spectra were conducted at open circuit potential (OCP), using the frequency range of 0.01 Hz to 100 kHz. The extracted parameters were calculated by using Z-View program software. All electrochemical tests were performed in 3.5 wt% NaCl in distilled water. Experiments were conducted after 7 days of immersion.

2.4. Complementary studies

Mechanical properties include hardness and reduced modulus were determined using nano-indentation technique (NanoTest Vantage, Micro Materials instruments).

Surface morphological studies of the coatings after 7.0 days of completed immersion in corrosive solution were evaluated using FE-SEM Model Quanta 250 (FEI Company, Netherlands).

2.5. Infrared spectrum

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Infrared spectrum of the title compound was recorded, as suspension powder in KBr, on a Perkin-Elmer Spectrometer 1750, in the range 4000–400 cm^{-1}.

3. Results and discussion

3. 1 Crystal structure

The structure of $(NH_4)_2[Mg(H_2O)_6]_3(HPO_3)_4$ was fully elucidated by Missouri et al. [18] and later reproduced by Abdellah et al. [19]. Its crystal structure is described as a framework made up of isolated $[Mg(H_2O)_6]^{2+}$, $[(HPO_3)]^{2-}$ and $[NH_4]^{+}$ groups that interconnect through an intricate network of hydrogen bonds (Fig. 1). Fig. 2 depicts projection of the crystal structure onto (001)-crystallographic plane.

3.2. IR study

Fig. 3 shows the IR spectrum of the title compound. The presence of P-H bonds is confirmed by IR-band band at 2440 cm^{-1}, which is ascribed to the stretching vibrations of P–H from the HPO_3. The bands in the region 1040–979 cm^{-1} indicate the deformation vibration of P–H bond [42,43], while those at 1260 cm^{-1} and 1064 cm^{-1} correspond to the stretching vibrations (νas) of PO_3 group. The vibrations of PO_3 groups appear as bands in the range of 620-450 cm^{-1}. The strong and broad band in the region 3550-3414 cm^{-1} is due to the stretching vibration of the water molecule and the NH_4^+ ion [44]. The intense bands at 1636 and 1617

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cm^{-1} are associated to the deformation vibrations of O–H bonds of water, and the bands at 1470 and1417 cm-1 are disturbed to the deformation vibrations of NH_4^+ group [45-46].

3.3. Evaluation of corrosion protection performance

Electrochemical impedance spectroscopy (EIS) has been exceedingly utilized as a non-destructive system to investigate the corrosion protection performance of coating [47]. In this part, the performance of epoxy-coated carbon steel in the absence and presence of different concentrations of MgHP immersed in 3.5% NaCl solution was assessed by assigning Nyquist plots (see Fig. 4). As shown in Fig. 4, the Nyquist plots for neat epoxy coating has consisted of two circuits capacitive loops. The two capacitive loops at high and low frequency are due to the resistance and capacitance of the epoxy coating and the steel-electrolyte interface, respectively [48]. Equivalent electric circuit with two time constants for neat epoxy coating was shown in Fig. 5. In this pattern, R_s is the solution resistance, R_p polarization resistance, C_{dl} the double layer capacitance at the metal and coating interface, R_{po} is the pore resistance and C_c is the coating capacitance.

The incorporation of 0.2% and 0.4% of MgHP increased the diameter of the two capacitive loops. This means that the addition of 0.2% and 0.4% of MgHP leads to enhance the anti-corrosion performance of epoxy

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coating, but still the efficiency of epoxy film not high to prevent the passage of corrosive ions into metal surface. The same equivalent electric circuit that used for describing the neat epoxy coating system can be used for fitting EIS data for epoxy coating containing 0.2% and 0.4% of MgHP (Fig. 5).

On the other hand, the significant changes in the anti-corrosion performance of epoxy coating were noticed with the change in MgHP concentration. The optimum coating performance was obtained at 0.8% and 1.0% concentration of MgHP. It is further seen that the incorporation of 0.8% and 1.0% concentration of MgHP has resulted in formation one time constant loop. The corresponding equivalent electric circuit can be presented in Fig. 6.

The fitted EIS parameters for epoxy-coated carbon steel in the absence and presence of different concentrations of MgHP are shown in Table 1. It has been reported from Table 1 that the incorporation of MgHP into the epoxy coating significantly increased R_{po},R_p and reduced C_c,C_{dl}, indicating enhanced coating performance in the presence of MgHP. Epoxy coatings generally diminish the corrosion of carbon steel liable to corrosive solutions in two procedures [49,50]. First, they act as a physical barrier film to control the entry of corrosive species. Second, they can serve as a reservoir for corrosion inhibitors to aid the steel surface in resisting attack by aggressive species. After a certain amount of time,

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corrosive ions penetrate into the coating and form a new liquid/metal interface under the coating. Corrosion phenomena can occur at this new interface.

In the case of neat epoxy coating, it is impossible to prevent enough moisture transmission through coating films to control the cathode reaction by moisture deprivation. The electrochemical reactions occurring at the defect points in the coating film can be summarizes in the following equations [51,52]:

$Fe(s) \rightarrow Fe^{2+}_{(aq)} + 2e$ anodic reaction (1)

$4e + 2O^{2}_{(aq)} + 2H_2O \rightarrow 4OH^{-}$ cathodic reaction (2)

The incorporation of MgHP with epoxy leads to formation of impermeable barrier coatings to suppress both oxygen transmission and the transmission of corrosion ions to a sufficient extent that corrosion may be impeded. This behavior is due to the fact that MgHP compound has great surface activity so it can absorb more epoxy resin on its surface. This enhances the density of the coating thereby reducing the transport paths for the corrosive electrolyte to pass through the coating system [53]. Moreover, the presence of Mg^{+2} ions in the structure of MgHP serves to prevent corrosion galvanically by acting as the anode of an electrochemical cell of which the steel substrate is the cathode [54]. This means that MgHP containing coatings gives a cathodic protection to the steel substrate.

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3.4. Water uptake of coating

Owing to the fact that the corrosion through coating system resulting from the contact between the substrate and the corrosive environment, the measurements of the water uptake of coating (W_c) is essential to determine the corrosion resistance of coating. The quantification of water uptake by a coating was derived from coating capacitance (C_c), according to Haruyama et al. [55].

$$W_c = [\log(C_t/C_0) / \log(\varepsilon_{H2O})] \times 100 \qquad (3)$$

where C_0 and C_t are respectively the initial capacitance and the one at a time t; ε_{H2O} being the dielectric constant of water at the working temperature.

The relative volume fraction of water uptake by a coating in the absence and presence of different concentrations of MgHP is plotted against the immersion period (see Fig. 7). As shown in Fig. 7, the coating film absorbed water rapidly at initial stage of immersion, and then the rate of water uptake showed only a slightly increase with time. It is clear that water uptake by epoxy coating decrease by the additions of MgHP compound. The amount of water absorbed into epoxy coating film is virtually dependent on the concentration of MgHP. The lowest amount was obtained at 1.0% concentration of MgHP. The low water uptake of epoxy coating containing MgHP compound, gives further support that the

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role of the MgHP in improving the anti-corrosive performance of these epoxy coatings [56].

3.5. Evaluation of mechanical properties

The mechanical properties of epoxy-coated carbon steel in the absence and presence of different concentrations of MgHP were inspected using the nano-indentation technique. From loading-unloading curves, hardness and reduced modulus of the coatings were determined and listed in Table 2 [31]. It clearly showed that the epoxy coating modified with MgHP offered a significantly enhanced hardness and reduced modulus of the coatings. The optimum hardness and reduced modulus were obtained at 1.0% concentration of MgHP. This behavior can be attributed due to two factors. First one, the MgHP particles tend to occupy pinholes and spaces in the epoxy coating, causing a reduction of the total free volume and an enhancement of the cross-linking density of the cured epoxy [34,57]. Second factor, MgHP particles prevent epoxy disaggregation during curing and result in a more homogenous coating [57].

3.6. Surface morphological studies

Typical SEM images of the epoxy-coated carbon steel in the absence and presence of different concentrations of MgHP after 7.0 days of completed immersion in 3.5% NaCl solution are shown in Fig. 8. As clearly seen in this figure, corrosive electrolyte penetration to the interface between the coating and the substrate took place. This caused

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weak adhesion between the coating and the substrate. Creaking in coating film was observable in the absence of MgHP. However, a small fractal flakes growth patterns was observed over the surfaces of the specimens coated with epoxy coating containing 0.2% and 0.4%. On other hand, the presence of 0.8% and 1.0% of MgHP improved significantly the texture of the epoxy coating. In addition, there are no blisters and/or pin-holes.

4. Conclusions

Crystals of $(NH_4)_2[Mg(H_2O)_6]_3(HPO_3)_4$ (MgHP) were synthesized by a wet chemistry route and characterized by IR spectroscopy. The effect of varying MgHP concentration on anti-corrosion and mechanical properties of epoxy coating has been studied. The EIS measurements indicated that the incorporation of MgHP particles increased the coating resistance and polarization resistance while reducing the coating capacitance and the double layer capacitance. Compared to neat epoxy resin, the epoxy coating containing MgHP particles exhibit better anti-corrosion and mechanical properties. The permeability of the epoxy coating can be adjusted by the loading and concentration of MgHP particles. The lowest water uptake by epoxy coating was obtained at 1.0% concentration of MgHP.

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Table 1: EIS parameters of epoxy-coated carbon steel in the absence and presence of different concentrations of MgHP immersed in 3.5% NaCl solution at 298K.

System	$R_{po} \times 10^{8}$ Ω cm^2	$C_c \times 10^{-11}$ F cm^{-2}	$R_p \times 10^{8}$ Ω cm^2	$C_{dl} \times 10^{-11}$ F cm^{-2}
Epoxy-coated	07.20	2.25	05.98	04.99
Epoxy-coated + 0.2% MgHP	15.02	1.02	22.20	02.32
Epoxy-coated + 0.4% MgHP	26.42	0.57	45.11	01.25
Epoxy-coated + 0.8% MgHP	39.95	0.35	-	-
Epoxy-coated + 1.0% MgHP	42.22	0.15	-	-

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Table 2: The hardness and reduced modulus of the coatings of epoxy-coated carbon steel in the absence and presence of different concentrations of MgHP.

System	Hardness (GPa)	Reduced modulus (GPa)
Epoxy-coated	0.132	2.89
Epoxy-coated + 0.2% MgHP	0.168	3.41
Epoxy-coated + 0.4% MgHP	0.187	3.78
Epoxy-coated + 0.8% MgHP	0.445	3.82
Epoxy-coated + 1.0% MgHP	0.699	4.20

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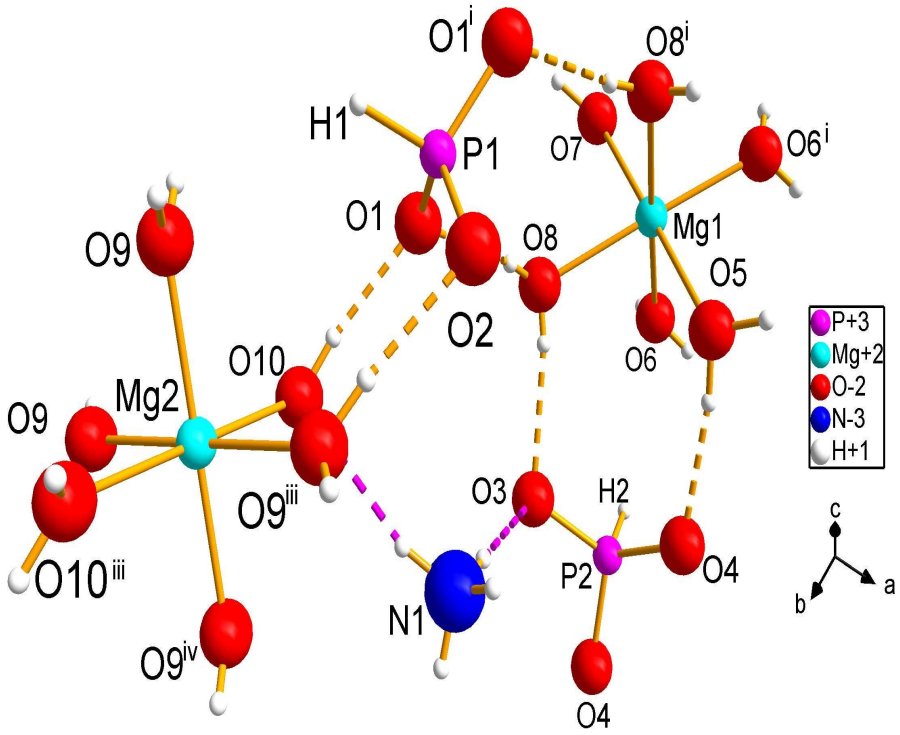

Fig.1

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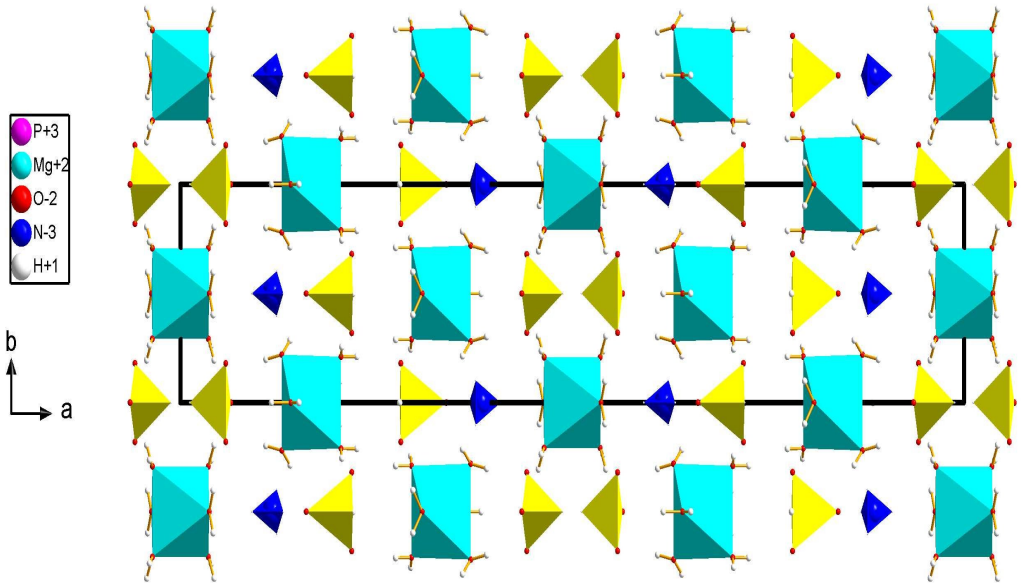

Fig. 2

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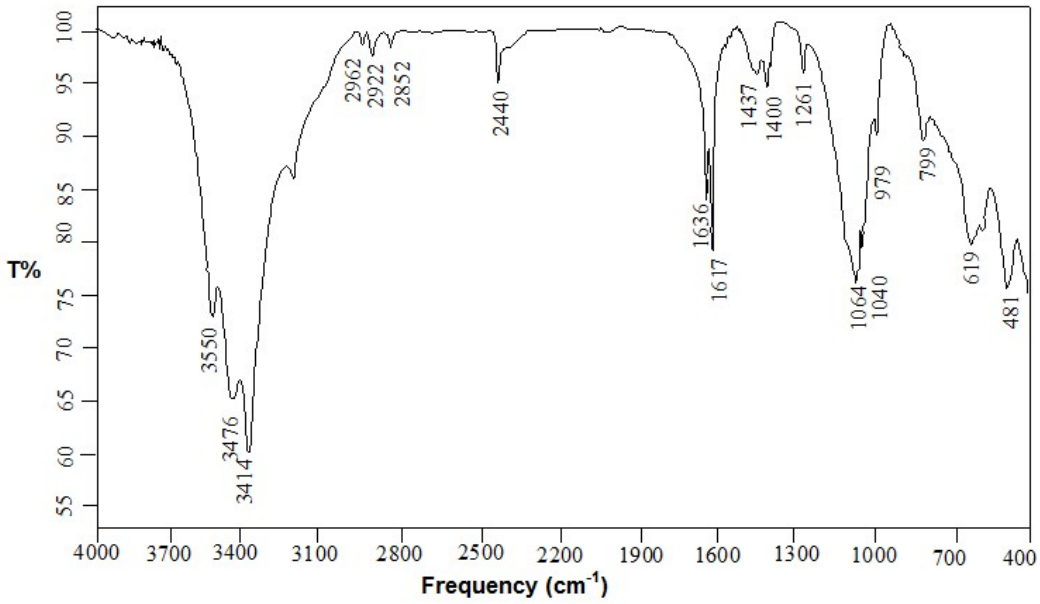

Fig.3

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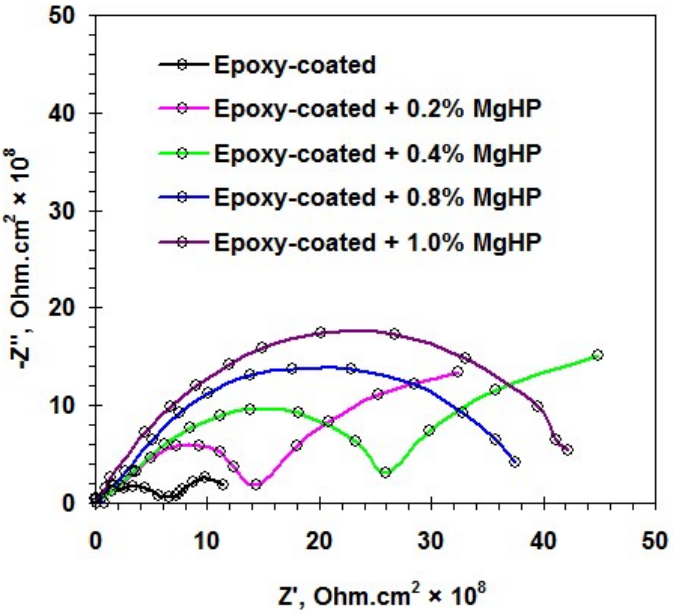

Fig. 4

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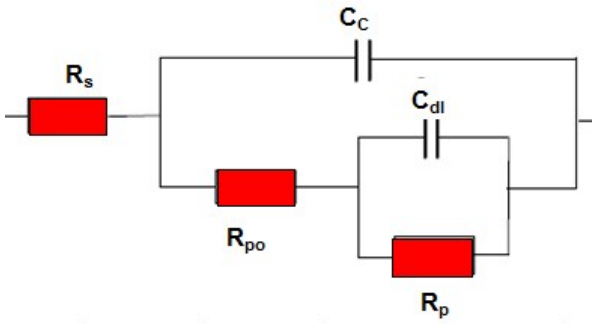

Fig. 5

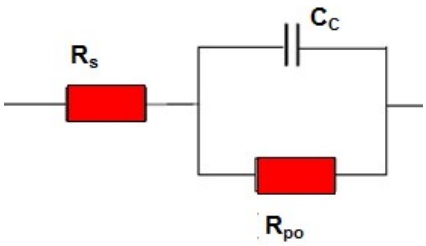

Fig. 6

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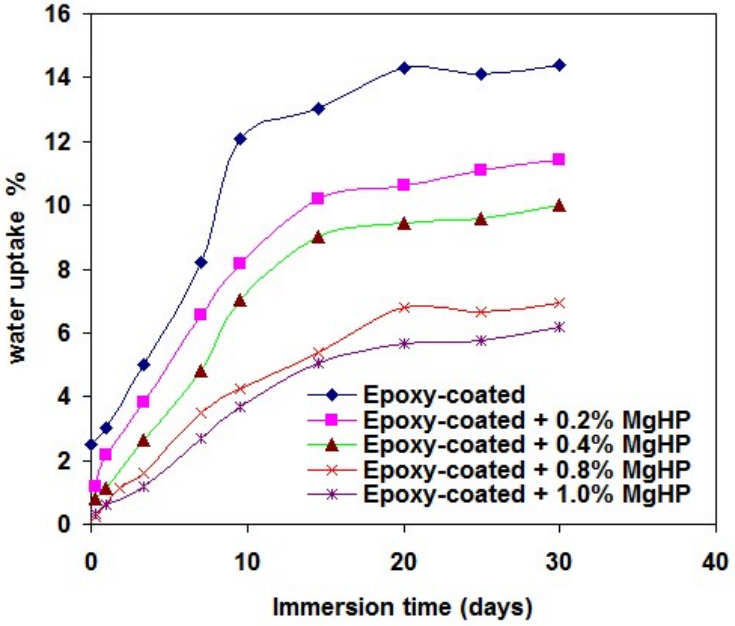

Fig. 7

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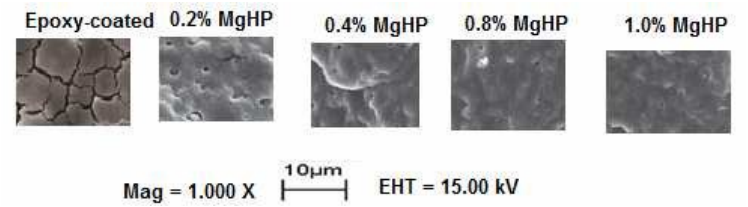

Fig. 8

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