

Smart epoxy coating containing Ce-MCM-22 zeolites for corrosion protection of Mg-Li alloy

Yanli Wang ^{*a, b}, Yanhao Zhu ^a, Chao Li ^a, Dalei Song ^a, Tao Zhang ^a, Xinran Zheng ^a, Yongde Yan ^a, Meng Zhang ^b, Jun Wang ^a, Dmitry G. Shchukin ^b

^a *Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China*

^b *Stephenson Institute for Renewable Energy Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK.*

Abstract

The epoxy coatings containing MCM-22 and Ce-MCM-22 zeolites were prepared by coating method on the Mg-Li alloy surface. The influence of MCM-22 and Ce-MCM-22 zeolites on corrosion protection of the epoxy coating was studied. The epoxy coating containing Ce-MCM-22 zeolites showed high corrosion resistance. Artificial defects in the epoxy coating containing Ce-MCM-22 zeolites on the Mg-Li surface were produced by the needle punching. The results show that the epoxy coating containing Ce-MCM-22 zeolites exhibits self-healing corrosion inhibition capabilities. It is ascribed to the fact that the Ce³⁺ ions are released from MCM-22

zeolites based on ion exchange of zeolite in the corrosion process of the Mg-Li alloy substrate. MCM-22 zeolites as reservoirs provided a prolonged release of cerium ions.

Keywords: MCM-22 zeolite; Cerium, self-healing; Corrosion, Mg-Li alloy

1. Introduction

Mg-Li alloys have been currently attracting intensive attentions in potential applications in automotive, aeronautics and electronic industries due to the low density, great strength-to-weight ratio, machining deformation, shock resistance and damping ability [1, 2]. However, Mg-Li alloys have the poor resistance to corrosion. Therefore, it is critical to improve the durability of Mg-Li alloys by suppression of the corrosion activity. Surface treatment is usually employed nowadays to improve the corrosion resistance of Mg-Li alloy, including chemical conversion coating [3, 4], anodic oxidation [5], electroplating [6, 7], micro-arc oxidation [8, 9], and deposition of the organic coating [10]. However, these methods only offer Mg-Li alloys a passive protection [11]. Once the passive coating is broken, water and salts can directly diffuse and reach the substrate through the damaged areas of the coating leading to corrosion propagation [12, 13]. Recently, an active protection was developed basing on controlled release of corrosion inhibitors from the reservoirs to cure the defects of the coating. These smart coatings have effective anticorrosion self-healing effects,

conferring the long-term corrosion protection of the substrate [12-15].

There has recently been considerable interest in developing zeolite in the fields of corrosion protection of metals due to its cation exchange, superior mechanical, thermal and chemical stability [16-21]. For example, the highly corrosion-resistant zeolites MFI coatings on Ti6Al4V alloys were reported by Rajwant S. Bedi [17]. Cooperation of mesoporous MCM-41 and Na-montmorillonite particles into the polymer matrix improved the corrosion resistance of epoxy resin [18]. In our previous work, the assembly ZSM-5 coatings prepared by hot-pressing provided good corrosion protection of Mg-Li alloy [19].

An increasing number of researchers are investigating MCM-22 zeolite which contains two-dimensional sinusoidal 10-membered ring (MR) apertures and 12-MR large supercages for unique ordered porous structure, especially its cation exchange [22-24]. Ce^{3+} ion is proven to an effective corrosion inhibitor [25, 26]. NaX zeolites used as reservoirs of Ce^{3+} ions enhanced the protective performance of the coating by cation exchange release [26]. However, cation exchange between MCM-22 and Ce^{3+} ion has rarely reported. Herein, we developed MCM-22 zeolites as reservoirs to load cation corrosion inhibitor - Ce^{3+} ions. The effect of Na^+ concentration on the release of Ce^{3+} ions from the MCM-22 zeolites was studied. The epoxy coating containing Ce-MCM-22 zeolites exhibited active corrosion protection properties. The self-healing properties of the epoxy coating containing Ce-MCM-22 zeolites were investigated with electrochemical impedance spectroscopy (EIS), scanning electron

microscopy (SEM) and energy-dispersive X-ray spectrum (EDS). The mechanism of the self-healing process was also proposed.

2. Experimental

2.1 Chemicals

The epoxy resin E44 with the epoxy equivalent of 212–243 g/equiv., was purchased from Wuxi Lanxing Epoxy Co., Ltd, China. The polyamide 615A was obtained from Beijing Xiangshan joint additives plant, China. The solvents including xylene, n-butanol and acetone were purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. Cerium nitrate hexahydrate was purchased from Guoyao Group of Chemical Reagents Ltd. Ammonium nitrate was purchased from Tianjin Quartz Clock Factory Bazhou Chemical plant. Hexamethyleneimine was obtained from Shanxi Province sheyang County Chemical Plant.

2.2 Substrate pretreatment

In this work, the substrate material was Mg-Li alloy (6.5 wt% Li, 3.5 wt% Al, 0.2 wt% Mn, 1.0 wt% (Zn+Sn) and Mg balance) synthesized by melting method. The Mg-Li alloy panels were carefully polished with 150, 400, and 1200 grit SiC paper,

cleaned ultrasonically using acetone for 10 min, and washed with an alkaline detergent at 60 °C for 15 min. Finally, the Mg-Li alloy panels were rinsed with distilled water and dried in air.

2.3 Preparation of the epoxy coating

MCM-22 zeolite was prepared using hexamethyleneimine as organic template as described in the literature [27]. In this study, Sodium hydroxide and sodium aluminate were firstly dissolved in deionized water. Then HMI and silica were added under vigorous stirring. The molar composition of the resultant mixture was $n(\text{SiO}_2):n(\text{Al}_2\text{O}_3):n(\text{NaOH}):n(\text{HMI}):n(\text{H}_2\text{O}) = 1:0.02:0.18:0.5:40$. After continuous stirring for 1 h, the mixture was transferred into a Teflon-lined autoclave, and was heated at 150 °C for 72 h. The resulting solid was filtrated, washed, dried, and calcined in air at 550 °C for 6 h to obtain MCM-22 zeolite. Then it was exchanged with a 2 M NH_4NO_3 by continuous stirring at 80 °C for 12 h. The resultant powder was filtered, washed with distilled water and dried, then calcined at 540 °C in air for 3 h. The above process was repeated twice. Ce-MCM-22 zeolite was synthesized by ion exchange method. MCM-22 zeolite was exchanged three times in a 0.1 M $\text{Ce}(\text{NO}_3)_3$ solution by continuous stirring at 80 °C for 24 h. The obtained samples were filtered, washed with distilled water, dried at 80 °C, and calcined at 540 °C in air for 3 h.

Zeolites (MCM-22 or Ce-MCM-22) were firstly added to the mixed solution of

xylene and n-butyl alcohol. Then the epoxy resins and polyamide were dissolved in the above mixture. The solution was stirred until the appropriate mixture was achieved. The mass ratio between epoxy resins/polyamide and xylene/n-butyl alcohol were 2:1 and 7:3, respectively. All samples were coated by the bar coating and cured at the room temperature for 24 h and 60 °C for 48 h. The thickness of the cured coatings was about 50 µm which was measured with a digital thickness gauge TT230.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on Rigaku D/max Ultima III diffractometer with Cu K α radiation operating at 40 kV and 150 mA in a 2 θ range of 5–40 °. SEM was carried out on JEOL JSM-6480A microscope combined with an energy-dispersive X-ray analysis (EDS).

To measure the release of Ce³⁺ ions from Ce-MCM-22 zeolites at different concentration of NaCl solution, these samples were prepared with a volume/solid ratio = 50 (mL/g) of Ce-MCM-22 zeolites and immersed in NaCl solution with the different concentration. After 48 h of immersion, the zeolites were filtered and dried. The cerium ion content in the zeolites was determined by inductively coupled plasma mass spectrometry (ICP-MS).

EIS was performed using Autolab PGSTAT302N electrochemical workstation, applying a 20 mV amplitude sinusoidal voltage in the 10⁵–10⁻² Hz frequency range. A

conventional three-electrode cell was employed containing a saturated silver/silver chloride (Ag/AgCl) as a reference electrode, a platinum foil as a counter electrode and Mg-Li substrate coated with the epoxy as a working electrode with the area of 1 cm². All measurements were conducted in a home-made Faraday cage in order to prevent electromagnetic interference.

Artificial defect was produced using needle (for EIS, SEM) with penetration to the Mg-Li alloy substrate. Corrosion performance of the scratched epoxy coating was evaluated by EIS, SEM and EDS after different immersion times (1 h, 20 h, 40 h and 120 h) in 0.35 wt % NaCl solution.

3. Results and discussion

The XRD patterns of the samples are displayed in [Fig. 1](#). These two samples show the characteristic diffraction peaks of the typical MWW structure which match well with MCM-22 zeolite reported in the literature [[27](#), [28](#)]. SEM micrographs of Ce-MCM-22 zeolites are depicted in [Fig. 2](#). Most of Ce-MCM-22 zeolites appear thin disk morphology with about 3-4 μm diameter.

[Fig. 3](#) displays the top view and cross-section of epoxy coating containing Ce-MCM-22 zeolites on Mg-Li alloy. The pictures show that relevant agglomerates are neither detected on the surface nor in the coating. The coating is relatively homogeneous, dense and crack free, suggesting a good compatibility between the

embedded Ce-MCM-22 zeolites with the epoxy matrix. The measured thickness of coating was approximately 50 μm , which is coherent with the thickness measured with a digital thickness gauge TT230.

The effect of concentration of Na^+ ions of as a trigger for Ce^{3+} ions release from cerium exchanged zeolites was studied to estimate the behaviour of exchanged zeolites in the epoxy coatings (Fig. 4). As the concentration of Na^+ increases from 0.35 wt% to 3.5 wt%, the ion-exchange degree of Ce^{3+} ions is increased from 20.5% to 66.6%. These results indicate that the release of Ce^{3+} ions from MCM-22 zeolites is favourable at high concentration of Na^+ ions in the solution.

The EIS data for the blank epoxy coating (a), epoxy coating containing MCM-22 (b) and Ce-MCM-22 zeolites (c) are displayed on the Bode plot as a function of immersion time, as shown in Fig. 5. The low-frequency impedance modulus can represent the corrosion protective properties of the coating [29, 30]. For the blank epoxy coating (see Fig. 5(a)), the low-frequency impedance values ($|Z|$) begin from $1.0 \times 10^7 \Omega \cdot \text{cm}^2$ (1 h), but decrease gradually to $2.4 \times 10^5 \Omega \cdot \text{cm}^2$ after 720 h immersion. The epoxy containing MCM-22 zeolites cannot maintain its impedance values, decreasing from $2.3 \times 10^7 \Omega \cdot \text{cm}^2$ to $5.6 \times 10^5 \Omega \cdot \text{cm}^2$ after 794 h of immersion (see Fig. 5(b)). However, for Ce-MCM-22 sample, the $|Z|$ value is about $9.8 \times 10^8 \Omega \cdot \text{cm}^2$ at the early period of immersion (Fig. 5(c)). After an initial drop to the value of $2.1 \times 10^7 \Omega \cdot \text{cm}^2$ (986 h), $|Z|$ value progressively increases to $1.4 \times 10^8 \Omega \cdot \text{cm}^2$ after 1492 h of immersion. Obviously, the epoxy coating containing Ce-MCM-22 zeolites

significantly improves corrosion resistance as compared with the blank epoxy coating and the epoxy coating containing MCM-22 zeolites, revealing effective long-term protection for the Mg-Li alloy.

Typical electrochemical impedance spectra of scratched epoxy coatings containing Ce-MCM-22 zeolites on the Mg-Li alloy substrate are shown in Fig. 6. Nyquist plots showed the impedance spectrum of the coating with two capacitive loops after 1 h immersion, indicating that the electrochemical reactions at the coating/metal interface can occur [31, 32]. High-frequency loop is related to the coating performance, and the low-frequency loop is attributed to the reactions occurring at the coating/Mg-Li alloy interface [31-33]. The barrier properties of the coating decrease with additional immersion time up to 20 hours. However, a rise in the coating resistance is clearly detected after 40 h of immersion suggesting that some ionic movement in the coating layer can be inhibited [32, 34]. Bode plots are displayed in Fig. 6b. When the immersion time increases from 1 h to 20 h, the impedance values at low frequency of the tested sample exhibits a decrease of about one order of magnitude. However, with further increasing the immersion time up to 40 h, the impedance value at low frequency greatly climbs, and almost keeps constant after 120 h immersion. These results indicate that an excellent barrier film formed on the scratched surface. The coating has good self-healing capabilities [35].

Fig. 7 shows optical photographs of scratched epoxy coatings containing MCM-22 and Ce-MCM-22 zeolites immersed in 0.35% NaCl solution after a 40

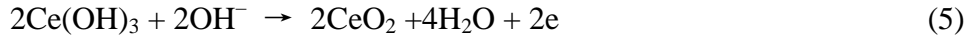
hours corrosion test. Upon 20 h of immersion, the filiform corrosion occurs under the epoxy coating with MCM-22 zeolites. For the epoxy coating containing Ce-MCM-22 zeolites, only a slight increase in the size of the scratched areas can be observed after 20 h immersion. Even after 40 h of immersion test, the scratched areas still looks smooth. The above results additionally confirm that the epoxy coating containing Ce-MCM-22 zeolites has the good self-healing protection ability for the substrate.

Fig. 8 shows SEM and Ce mapping analysis images of scratched epoxy coating containing Ce-MCM-22 zeolites immersed in 0.35% NaCl solution at various times. After 1 h of immersion, Ce is still uniformly distributed on the surface of epoxy coating. After 40 h of immersion, more and more Ce migrates to the scratched areas, reflecting the release of Ce^{3+} from the MCM-22 zeolites. To evidently observe the self-healing properties of the coating, the coating was peeled away from Mg-Li alloy for the scratched sample after 120 h of immersion and a large amount Ce precipitates further deposited on the scratched areas of the substrate.

[Scheme 1](#) represents the self-healing effect of the coating. In general, the electrochemical process of magnesium alloy can be described as follows [36]:



Consequently for the released Ce^{3+} ions from the MCM-22 zeolite, the following reactions occur [37]:



The presence of Ce^{3+} ions in the coating is ascribed to the higher cation concentration based on cation exchange properties of the MCM-22 zeolite [26]. The hydroxyl groups origin from the cathodic reaction according to the reactions 3-5 [38]. The presence of the precipitation of CeO_2 was attributed to the interaction of the Ce^{3+} ions and the hydroxyl groups according to the reaction 4-5. Therefore, the Ce inhibition process is mainly triggered by the increase of concentration of hydroxyl groups in corrosion places. The stable precipitation of CeO_2 progressively delays the corrosion activity, particularly hindering the cathodic reaction and providing with effective coverage on the scratched areas.

4. Conclusions

The epoxy coating containing Ce-MCM-22 zeolites exhibits a better corrosion resistance performance, as compared with the blank epoxy coating and the epoxy coating containing MCM-22 zeolites. MCM-22 zeolites as reservoirs of active species Ce^{3+} completely avoided the spontaneous leakage of Ce^{3+} ions during the coating forming process. The self-healing properties of the epoxy coatings containing Ce-MCM-22 zeolites were demonstrated based on the corrosion of scratched samples by EIS, SEM and EDS measurements in a 0.35% NaCl solution. The active Ce^{3+}

species are released from MCM-22 zeolites due to ion-exchange properties of zeolite and precipitated to the scratched areas of the Mg-Li alloy. So the smart epoxy coating containing Ce-MCM-22 zeolites provides effective long-term active protection for the magnesium.

Acknowledgements

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Captions for the figures

Fig.1 XRD patterns of MCM-22 and Ce-MCM-22 zeolites.

Fig2. SEM images of the Ce-MCM-22 zeolites.

Fig.3 SEM images of top view and cross-section of epoxy coating containing Ce-MCM-22 zeolites on Mg-Li alloy.

Fig.4 Release of Ce^{3+} from Ce-MCM-22 zeolites as function of concentration of NaCl solution.

Fig.5 Bode plots of the blank epoxy coating (a), Epoxy coating containing MCM-22 (b) and Ce-MCM-22 (c) immersed in 3.5% NaCl solution after different immersion times.

Fig.6 Nyquist (a) and Bode plots (b) of scratched epoxy coatings containing Ce-MCM-22 immersed in 0.35% NaCl solution after different immersion times.

Fig.7 optical photographs of scratched epoxy coatings containing Ce-MCM-22 (a, b, c) and MCM-22 (d, e) zeolites immersed in 0.35% NaCl solution at different immersion times. a, d: 1 h; b, e: 20 h; c: 40 h.

Fig. 8 SEM and Ce mapping analysis images of scratched epoxy coating containing Ce-MCM-22 immersed in 0.35% NaCl solution at different immersion times (a, b: 1 h; c, d: 40 h; e,f 120 h) . Note: the coating was peeled away from Mg-Li alloy for the scratched sample after 120 h immersion before scanning.

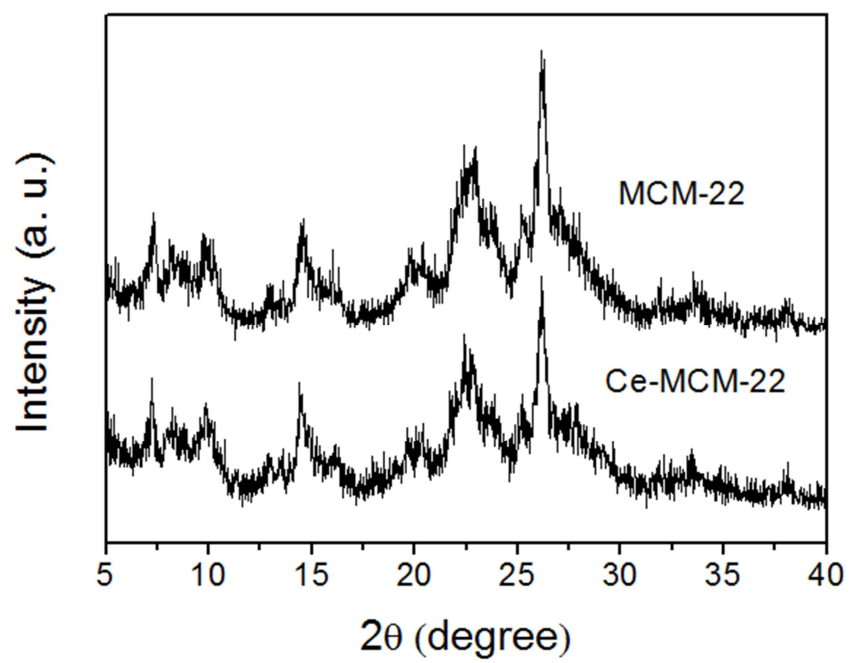


Fig.1

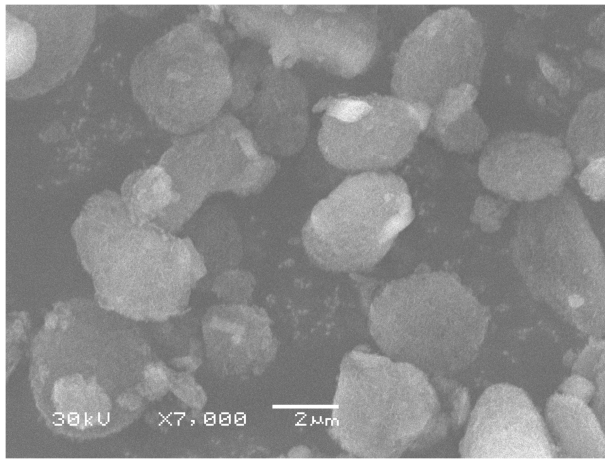


Fig.2

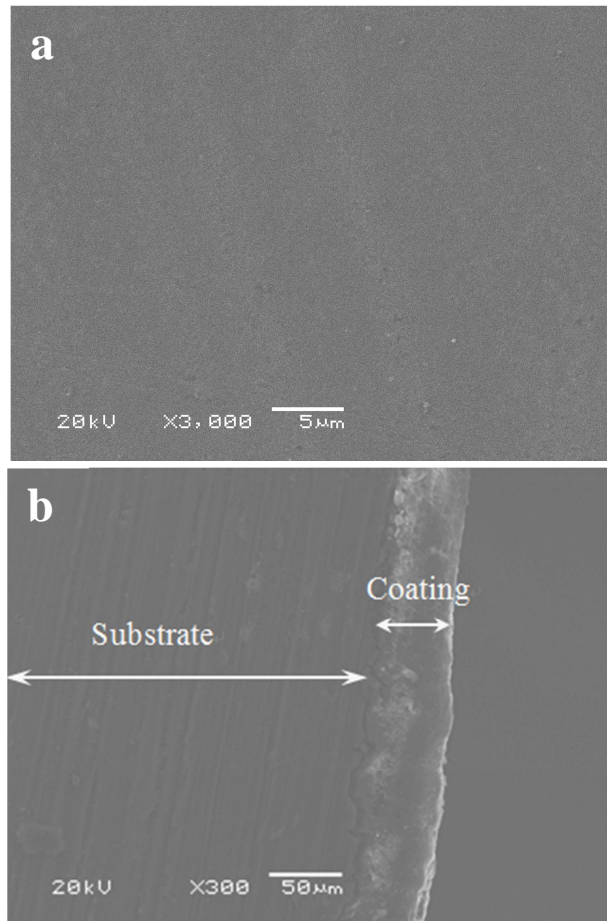


Fig.3

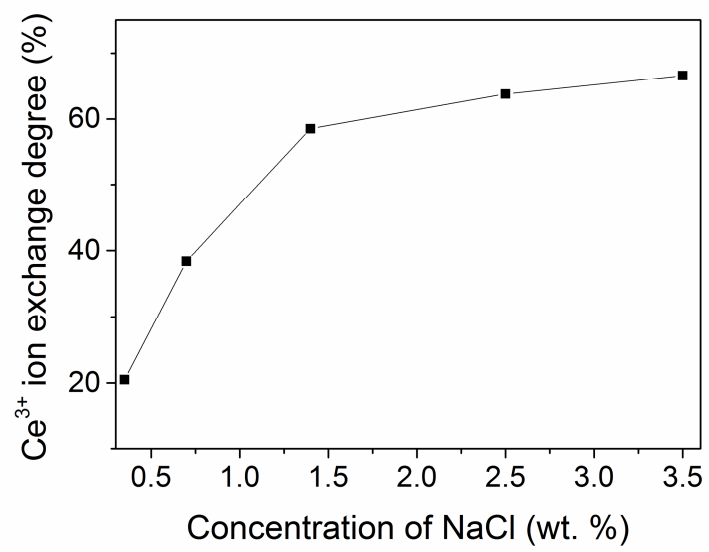


Fig.4

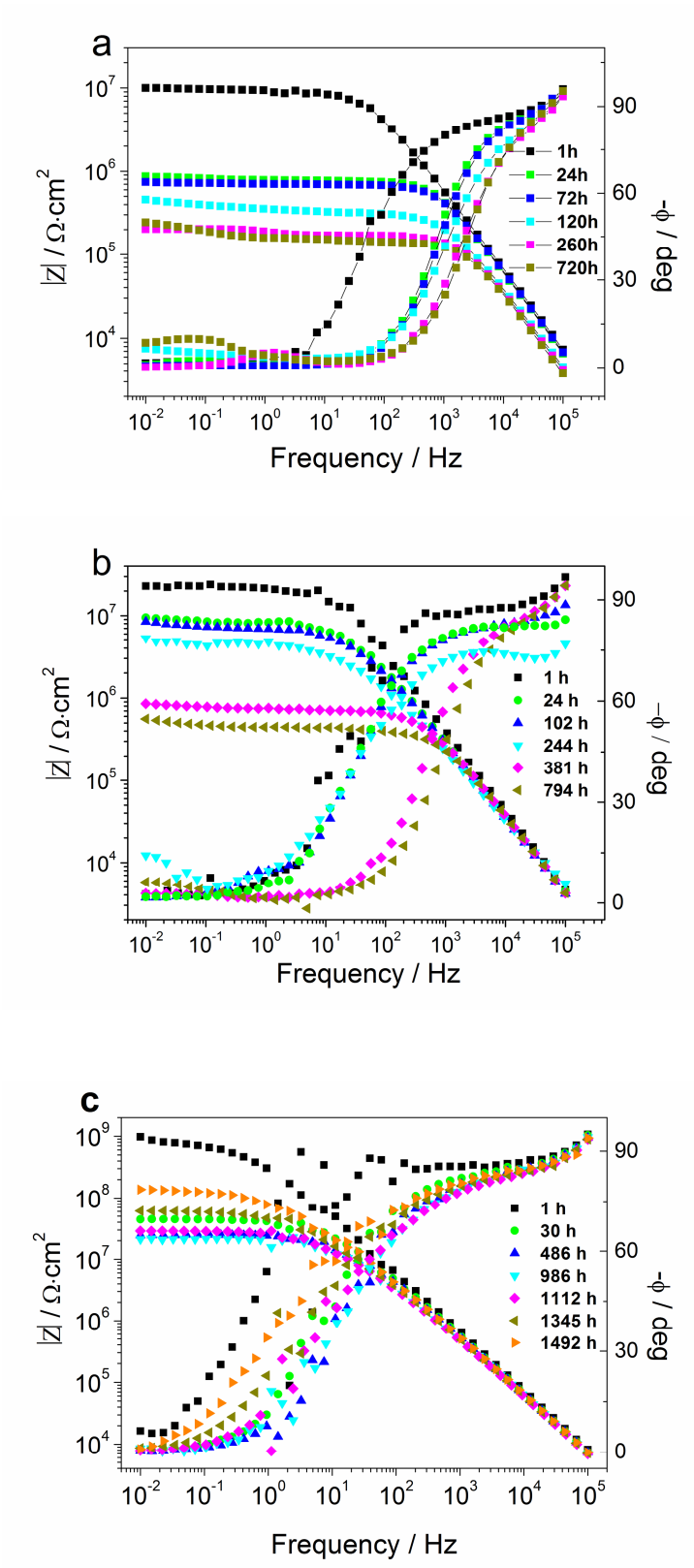


Fig. 5

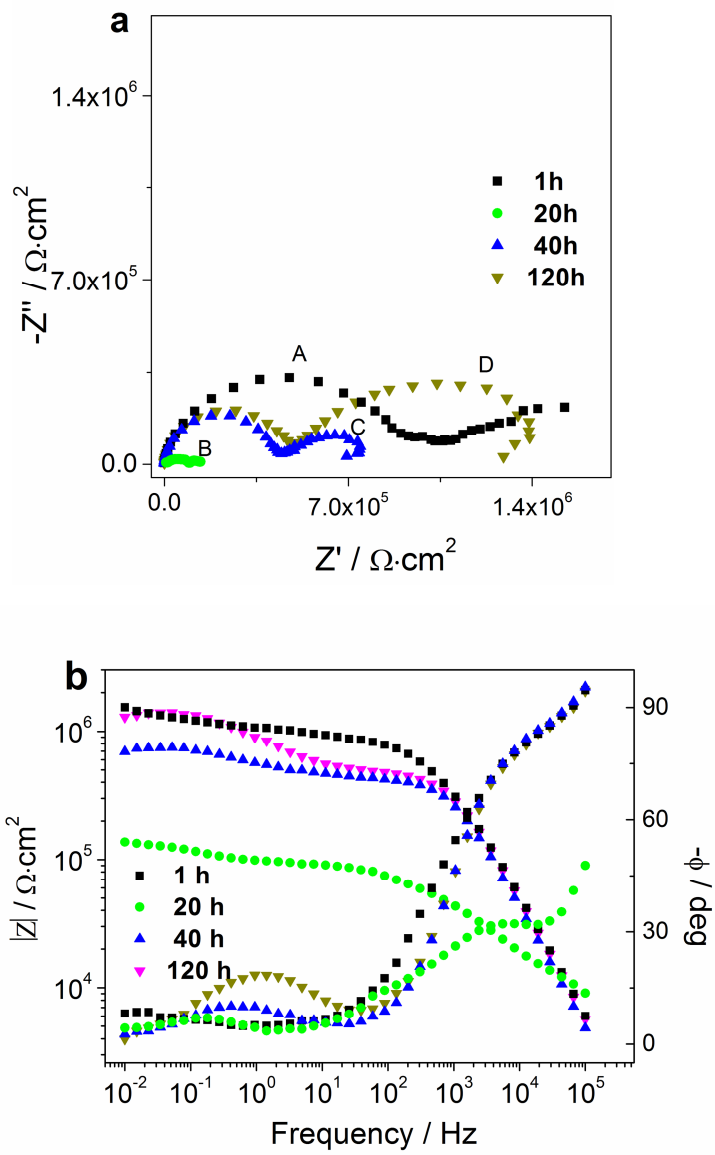


Fig.6

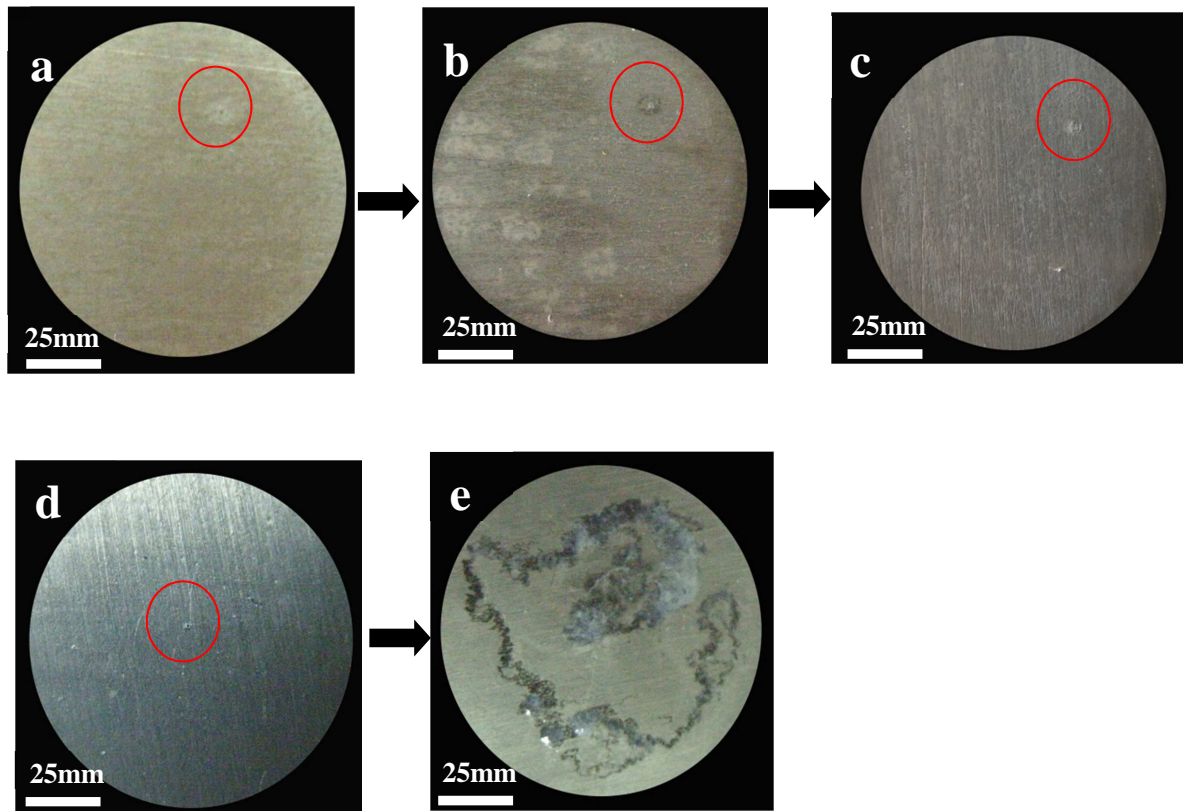


Fig.7

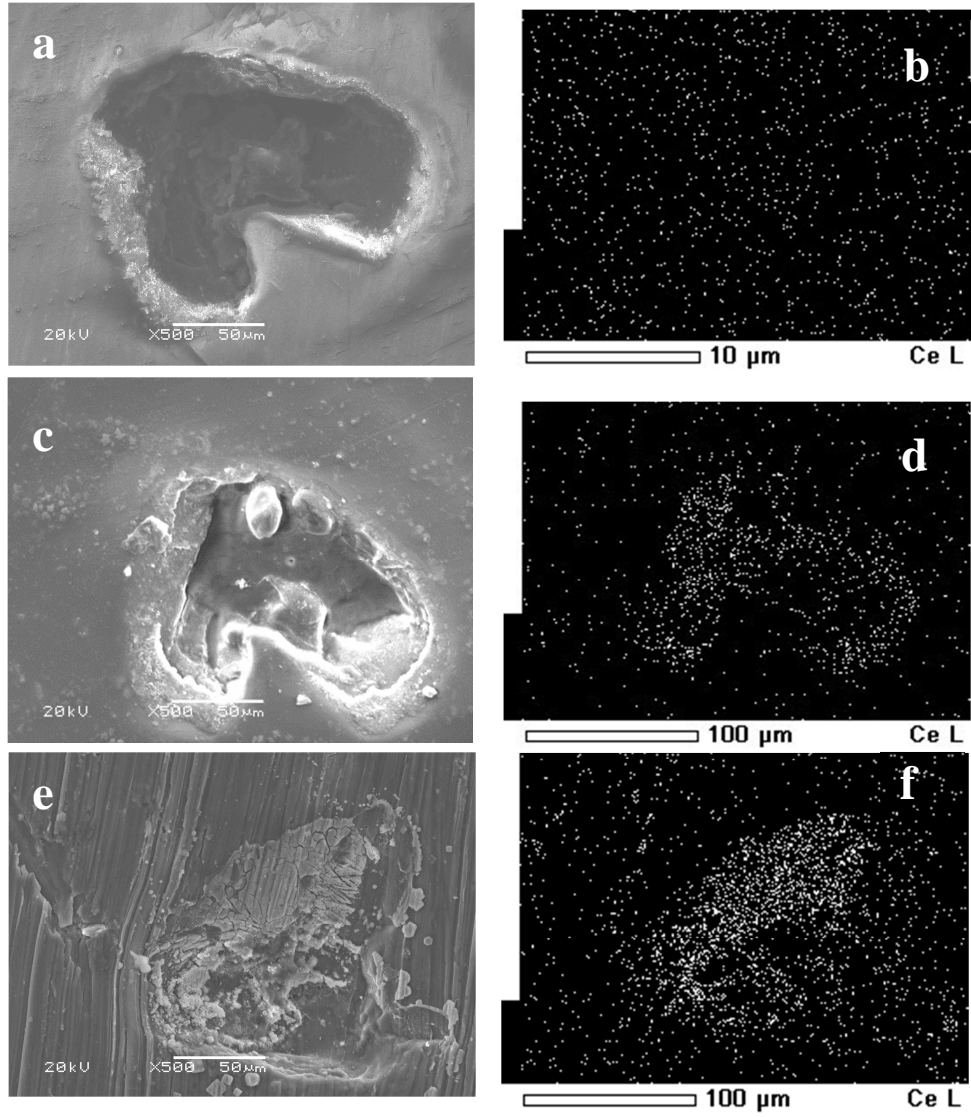
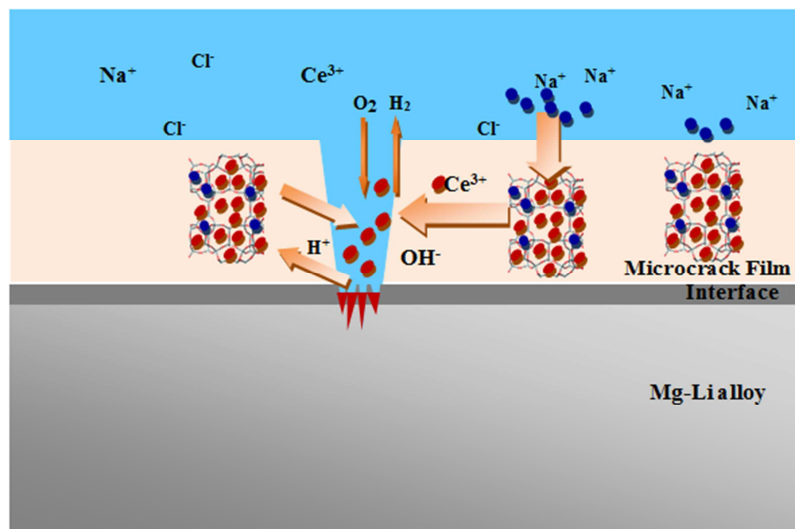


Fig.8



Scheme 1. Schematic representation of the stimuli-triggered release process in the epoxy coating containing Ce-MCM-22 zeolites.