

Effect of polypyrrole coating modified by sodium fluoride and polyethylene glycol on corrosion behaviour of AZ31 magnesium alloy

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A polypyrrole (PPy) coating modified by sodium fluoride (NaF) and polyethylene glycol 4000 (PEG) on AZ31 magnesium alloy is reported. The aim of this work was to obtain a composite coating with NaF and PEG in PPy matrix by electropolymerisation process. The idea was to form a stable PPy coating with higher resistance to corrosion damage. Prior to this process, the effect of sodium salicylate pre-treatment on PPy electropolymerisation was investigated by cyclic voltammetry technique. Electrochemical impedance spectroscopy (EIS) and polarisation analysis was performed in 0.05 M NaCl solution to characterise the corrosion behaviour of each sample. EIS results showed that the addition of NaF and PEG could enhance the corrosion resistance (R_{ct}) of PPy coating. Also, the corrosion current density for NaF + PEG (incorporated in PPy) was demonstrated a value 60 times lower than that of bare AZ31 Mg alloy. The better corrosion behaviour of PPy composite coating with NaF and PEG was attributed to inhibition effect of fluoride which could act as barrier for Mg alloys. Moreover, PEG can stabilise the PPy structure because of its high oxygen content. Furthermore, the addition of NaF and PEG simultaneously could show a synergistic behaviour because of the positive effect of PEG on fluoride mobility.

1. Introduction: Magnesium (Mg) alloys have a wide range of potential applications considering rich resources of Mg ore, low density, and high strength/weight ratio [1]. However, extensive applications of Mg alloys are limited by high chemical activity and rapid dissolution in atmospheric conditions [2]. Several methods have been developed to overcome these issues, such as using alloying elements [3] or protective coatings [4]. However, the low solubility of many metals in Mg leads to the formation of the second phase that could play as a cathode region in the Mg alloy and deteriorate its corrosion resistance [5]. Hence, it seems that the application of coatings is a superior option for Mg alloys protection because of its barrier properties.

In recent years, conducting polymers (CPs) have been used for corrosion protection of Mg alloys. CPs are electrically conductive material [6]. This feature allows direct formation of CPs by electropolymerisation process on the Mg alloys surface [7]. As a conductive polymer, polypyrrole (PPy) is easily synthesised and stable [8]. Electropolymerisation of PPy should be applied with a suitable anion in the solution that forms the complex compound with the Mg ions, leading to the protection against active dissolution because of the formation of the passive layer. According to the literature [9], salicylate compounds such as sodium salicylate ($C_7H_5NaO_3$) are the most appropriate candidate that allows the formation of an adherent and homogeneous PPy film.

Only little information on the direct electrochemical deposition of PPy on Mg surfaces is available. However, it is proven that by doping the inorganic materials within the PPy film, mechanical and corrosion properties of coatings are considerably improved [10].

A polypyrrole/polyethylene glycol (PPy/PEG) composite coating was proposed for platinum [11], ITO [12], and titanium [13]. However, to the best of our knowledge, there is a lack of information about the deposition of PPy/PEG coating onto Mg alloys. Nevertheless, it is indicated that in the presence of PEG in the solution, a lower charge for PPy electropolymerisation is needed in comparison with the absence of PEG [14].

In addition, it is observed that fluoride could act as a corrosion inhibitor for protection of Mg alloy in the corrosive solution [15]. In this Letter, we modified the PPy film with PEG and sodium fluoride (NaF) to improve the corrosion resistance of PPy coating.

2. Experimental: Commercially available AZ31 Mg alloy (3% aluminium and 1% zinc) was cut into $30 \times 20 \times 3$ mm samples and then polished by #80–#1200 abrasive papers, cleaned in ethanol/acetone 1:1 for 10 min and then rinsed with distilled water and dried in a stream of warm air. The pyrrole (Py) monomer (for synthesis), sodium salicylate ($C_7H_5NaO_3$), and PEG 4000 (4000 molecular weight) were purchased from Merck.

Before electropolymerisation, passivation of AZ31 Mg alloy was carried out through the cyclic voltammetry (CV) in the 0.5 M sodium salicylate aqueous solution in the sweeping potential of -0.6 to 1.2 V at 10 mV/s scan rate for two cycles. Finally, PPy films were electropolymerised on AZ31 Mg alloy samples in the aqueous solution containing 0.25 M Py and 0.5 M sodium salicylate using CV in the potential region between 0 and $+1.2$ V at 20 mV/s scan rate for ten cycles.

PAR EG&G potentiostat/galvanostat 273 model was used for electropolymerisation by CV technique. The electrochemical measurements were carried out in a classical electrochemical cell with an AZ31 sheets as working electrode with an exposed area of 4 cm². A platinum plate was used as the counter electrode, while a saturated calomel electrode (SCE) was taken as a reference electrode. Py used for the electropolymerisation was distilled twice and kept refrigerated in the dark before coating procedure.

Additionally, electropolymerisation of PPy on AZ31 Mg alloy in solution containing different proportions of PEG (10, 25, and 50 wt.% to PPy) and different concentrations of NaF (30, 80, and 150 ppm) was performed to investigate their contribution to the corrosion resistance of PPy coating.

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation tests were performed after 60 and 120 min of immersion in 0.05 M NaCl solution, respectively. The exposed area for these experiments was chosen to be 1 cm². EIS measurements were carried at the open circuit potential (OCP) potential with 5 mV AC amplitude over the frequency range from 100 to 10 mHz using a 1260 Solarton frequency response analyser. All potentiodynamic polarisation tests were carried out after stabilising the OCP in the chloride media. An EG&G potentiostat–galvanostat 273A model instrument, controlled by the PowerSuite software, was used to conduct potentiodynamic polarisation tests. The potential

was scanned from -400 to 400 mV versus SCE at a scan rate of 1 mV/s. All electrochemical tests were performed three times to ensure data accuracy.

3. Results and discussion: Prior to the electrochemical polymerisation of Py monomer, a pre-treatment passivation process is needed to improve adhesion and uniformity of PPy film [16]. Fig. 1a shows the CV of AZ31 Mg alloy obtained in a monomer free 0.5 M sodium salicylate solution. The passivation process was conducted with the sweeping potential of -0.6 to 1.2 V at a fixed scan rate (10 mV/s) for two cycles. Next, PPy coating was electropolymerised on the passivated surface of AZ31 in the electrolyte containing 0.5 M sodium salicylate with 0.25 M pyrrole (Py) by CV (0 – 1.2 V) at a fixed scan rate (20 mV/s) for ten cycles. It should be noted that at the higher scan rate of electropolymerisation, Py monomer does not have enough time to approach the electrode surface so that PPy film does not form properly. Furthermore, the high anodic dissolution of Mg at the lower scan rate does not allow polymerisation of Py monomer on the surface [17]. As shown in Fig. 1a, the Mg surface is highly active at the beginning of the first cycle (potential range between -0.6 and 0 V) due to the severe anodic dissolution. As presented in this figure, the recorded current density is about 30 mA/cm². A drop in current density in the potentials around 0 V might be attributed to the reduction of anodic dissolution of Mg. A decrease in the current density observed at the end of the first half cycle is related to the salicylate oxidation on the Mg surface. The peak was also observed in a reverse direction around 1.1 V, which may emphasise the reduction of sodium salicylate. This reversible redox couple could be indexed to the oxidation–reduction of sodium salicylate [18]. In the beginning of the

second cycle, the lower current density was observed in comparison with the first cycle, implying the partial passivation of the Mg surface in the presence of salicylate [9].

Fig. 1b shows the first cycles of PPy electropolymerisation on AZ31 alloy with and without pre-treatment by sodium salicylate. As shown in this figure, the application of salicylate pre-treatment leads to the lower activity of AZ31 Mg alloy and lower current density with consequent better electropolymerisation of PPy. This behaviour is observed in the first part of anodic direction within the potential range up to 0.8 V (solid line). By exceeding this potential, a drop in current density occurs probably due to the overlapping of two peaks. This phenomenon might be due to the electropolymerisation of salicylate with Py monomer simultaneously. Thus, the oxidation peak of Py is not observed due to merging with the oxidation peak of salicylate ions [17, 18].

Without the application of salicylate pre-treatment on AZ31, a sharp rise in electropolymerisation current is observed after 0.9 V because of the higher oxygen evolution at the surface [19]. As seen in Fig. 1b, the current density at the higher potentials is lower for salicylate treated AZ31. It seems that pre-treatment on Mg surface leads to the higher surface coverage after electropolymerisation. Therefore, Mg cannot be dissolved as effective as the untreated surface.

Figs. 2a–b demonstrate the top surface of the PPy-coated AZ31 with and without salicylate pre-treatment. As shown in Fig. 2a, the surface pre-treatment by salicylate creates smoother and more homogeneous PPy coating. Moreover, the untreated surface (Fig. 2b) shows more blisters after electropolymerisation probably due to the higher oxygen evolution on the surface of Mg electrode.

Therefore, all experiments were conducted on the pre-treated AZ31 Mg alloy surface.

Fig. 3 shows the Nyquist EIS spectrum for bare AZ31 alloy and samples coated by PPy in 0.05 M NaCl solution after 1 h immersion. Inductive loops are present at the low-frequency regions for both spectra. These loops are explained by presence of relaxation process of adsorbed species such as $\text{Mg}(\text{OH})_{\text{ads}}^+$ or $\text{Mg}(\text{OH})_{2\text{ads}}$ [20], pitting [21], hydroxide formation such as gelatinous film from $\text{Mg}(\text{OH})_2$ and its derivatives [22], and partial protection of oxide film on the surface [23]. The first observed semi-circle

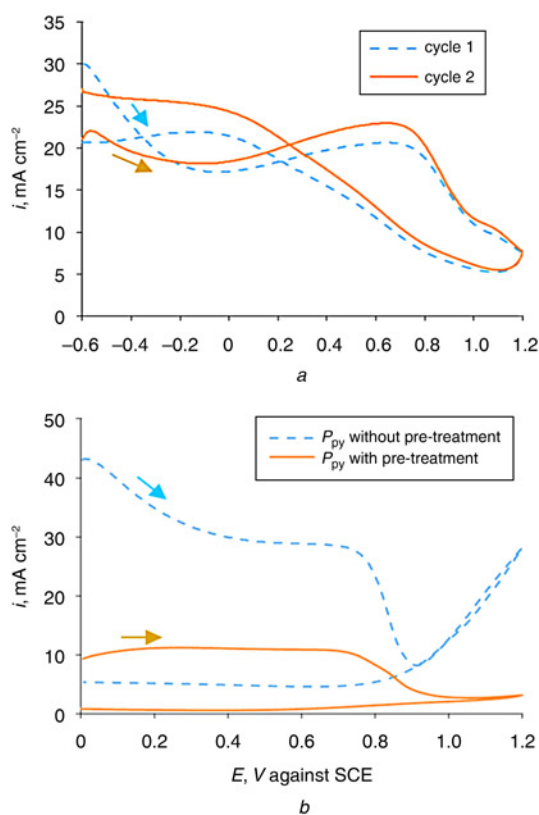


Fig. 1 CV of AZ31 Mg alloy and first voltammetry cycles of PPy film electropolymerisation on AZ31 Mg alloy
a CV of AZ31 Mg alloy in 0.5 M sodium salicylate of a monomer free solution
b First voltammetry cycles of PPy film electropolymerisation on AZ31 Mg alloy with and without pre-treatment by sodium salicylate



Fig. 2 PPy film electropolymerised on AZ31 Mg alloy
a With sodium salicylate pre-treatment
b Without sodium salicylate pre-treatment

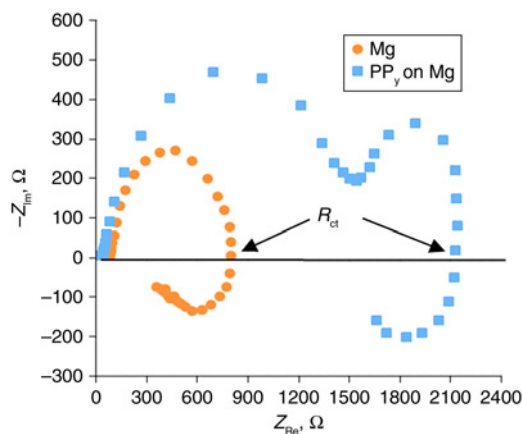


Fig. 3 Nyquist plots of bare and PPy-coated AZ31 alloy samples after immersion in 0.05 M NaCl solution for 1 h

formed at the high-frequency regions of coated AZ31 alloy relates to the presence of PPy film on the surface. The second loop in medium-frequency regions corresponds to the capacitance behaviour of Mg surface that is created due to the formation of porous PPy and relatively easy penetration of electrolyte through the coating [24]. It should be noted that the corrosion resistance of Mg decreased due to the presence of porous PPy layer on the surface. Charge transfer resistance (R_{ct}) values were determined based on the data presented in Fig. 3. R_{ct} value for PPy-coated AZ31 alloy is higher than that of bare AZ31 because of the corrosion resistance of PPy film. R_{ct} is defined as the value corresponding to Z' when $-Z'' = 0$, which is commonly obtained at intermediate frequencies [15]. Therefore, R_{ct} values for PPy-coated AZ31 alloy and bare Mg were estimated about 2120 and 790 $\Omega \text{ cm}^2$, respectively.

Fig. 4 illustrates polarisation measurement data for bare AZ31 alloy and PPy-coated samples in 0.05 M NaCl solution after 2 h immersion. As observed in this figure, the related curve for PPy-coated AZ31 alloy shows a higher corrosion resistance due to the lower I_{corr} [25]. The estimated I_{corr} values for PPy-coated AZ31 alloy and bare Mg were 50 and 180 $\mu\text{A cm}^{-2}$, respectively. The increase in the corrosion potential could be explained by the semi-barrier effect of PPy film lowering the anodic dissolution rate of AZ31 [25]. The E_{corr} values for PPy-coated AZ31 alloy and bare Mg were -1.42 and -1.53 V against SCE, respectively. Besides, as seen in this figure, PPy-coated AZ31 alloy at anodic potentials

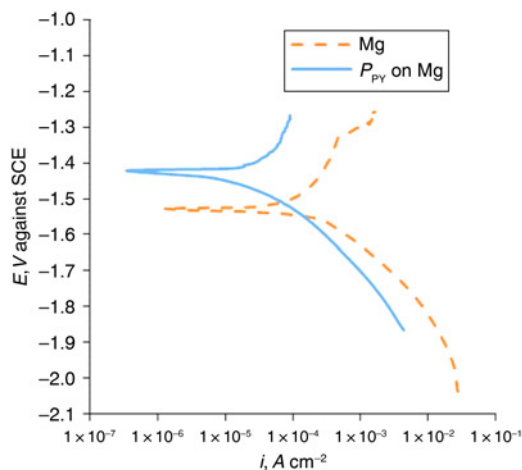


Fig. 4 Polarisation curve of bare and PPy-coated AZ31 alloy samples after immersion in 0.05 M NaCl solution for 2 h

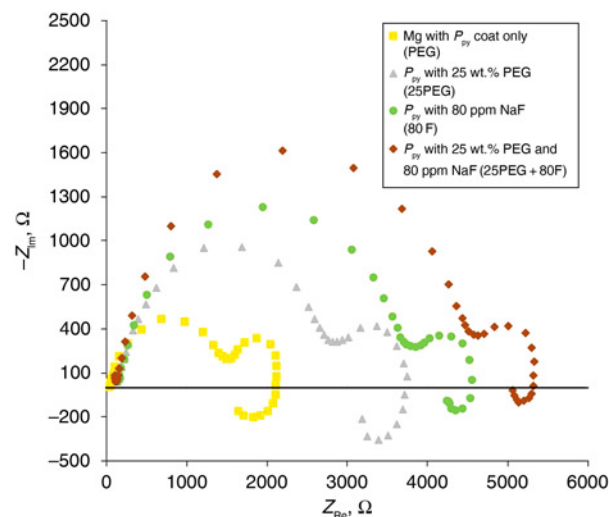


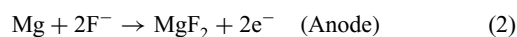
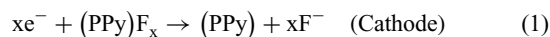
Fig. 5 Nyquist plots of PPy-coated AZ31 alloy with and without additives after immersion in 0.05 M NaCl solution for 1 h

shows a much lower current in comparison with the bare Mg probably because of the resistance behaviour of PPy film at high anodic potentials [9].

In the next step, PEG in 10, 25, and 50 wt.% to PPy and NaF in 30, 80, and 150 ppm were added to the polymerisation solution to investigate their effect on corrosion behaviour of PPy coating in 0.05 M NaCl solution. The best results were obtained in PEG (25 wt.% to PPy), 80 ppm NaF, and PEG (25 wt.% to PPy) + 80 ppm NaF which was denoted in this Letter as 25PEG, 80F, and 25PEG + 80F, respectively.

Fig. 5 illustrates the EIS results for PPy composite films with 25PEG, 80F, and 25PEG + 80F. As shown in this figure, by the addition of PEG or/and fluoride the corrosion resistance of PPy coating becomes greater than that of the blank PPy. The obtained R_{ct} values for PPy, 25PEG, 80F, and 25PEG + 80F are 2120, 3738, 4550, and 5322 $\Omega \text{ cm}^2$, respectively.

In the case of using fluoride, the high potential between the fluoride and Mg ions due to the high electronegativity and low weight of fluoride leads to the powerful attraction and strong adsorption of fluoride ions on the surface of Mg [26]. In this case, the released fluoride anions from the PPy structure migrate through the matrix and react with Mg ions in the anode to form stable magnesium fluoride layer. The following reactions are suggested during this process at the interface of Mg/PPy [27]:



Furthermore, in the case of using PEG during the synthesis of PPy coating, a large amount of PEG is incorporated into the PPy and a more compact structure is attained [28], hindering the penetration of aggressive ions. Therefore, the barrier effect of PPy coating was improved. Also, according to the literature [29], the presence of PEG into the PPy coating improves its mechanical stability and adherence due to the formation of coating with lower particle size. That confirmed our observation about its positive effect on corrosion behaviour of PPy/PEG composite coating.

Interestingly, PEG and fluoride have synergistic behaviour. Results (Fig. 5) indicated that the corrosion resistance (R_{ct}) for mixed case (25PEG + 80F) was better than in both cases when those components were used individually. The synergistic mechanism between PEG and NaF is ambiguous but Schreiber *et al.* [29] have found that the PEG facilitates the mobility of ions into the

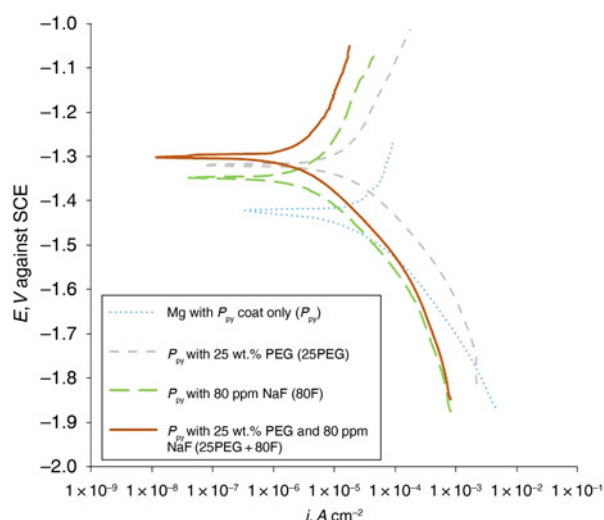


Fig. 6 Polarisation curve of PPy-coated AZ31 alloy with and without additives after immersion in 0.05 M NaCl solution for 2 h

film because of the abundant oxygen in its molecule. This feature allows fluoride to easily move around the coating.

Finally, polarisation measurement was performed for PPy composite films with 25PEG, 80F, and 25PEG + 80F. As presented in Fig. 6, the curve for 25PEG + 80F shows the lowest I_{corr} in comparison with other samples, meaning a higher corrosion resistance [25]. The estimated I_{corr} values for PPy, 25PEG, 80F, and 25PEG + 80F are 50, 15, 5, and 3 $\mu\text{A cm}^{-2}$, respectively. Corrosion current density of 25PEG + 80F demonstrates a value 60 times lower than that of bare AZ31 Mg alloy which predicts considerable better corrosion resistance.

4. Conclusion: Electropolymerisation of PPy with or without passivation pre-treatment by sodium salicylate was performed by CV technique on the AZ31 Mg alloy. The results confirmed with the passivating process, the Py monomer shows a better deposition behaviour, and more stable PPy film could be formed. In the next step, during the electropolymerisation process, the addition of some component to PPy matrix such as PEG or sodium led to the better corrosion property of composite PPy coating by 60 times in comparison with bare Mg. According to the results of this work, fluoride react with Mg most probably and form stable magnesium fluoride layer to inhibit corrosion damage. Furthermore, incorporating PEG into the PPy provides a more compact structure that prevents the aggressive ions receiving the Mg substrate. Finally, the observed synergistic behaviour of 25PEG + 80F can be attributed to intrinsic PEG and fluoride features.

5 References

- [1] Song G., Stjohn D.: 'Corrosion behaviour of magnesium in ethylene glycol', *Corros. Sci.*, 2004, **46**, pp. 1381–1399
- [2] Sheng N., Ohtsuka T.: 'Preparation of conducting poly-pyrrole layer on zinc coated Mg alloy of AZ91D for corrosion protection', *Prog. Org. Coat.*, 2012, **75**, pp. 59–64
- [3] Zberg B., Uggowitzer P.J., Löffler J.F.: 'MgZnCa glasses without clinically observable hydrogen evolution for biodegradable implants', *Nat. Mater.*, 2009, **8**, (11), pp. 887–891
- [4] Gray J.E., Luan B.: 'Protective coatings on magnesium and its alloys – a critical review', *J. Alloys Compd.*, 2002, **336**, (1–2), pp. 88–113
- [5] Biribilis N., Williams G., Gusieva K., *ET AL.*: 'Poisoning the corrosion of magnesium', *Electrochem. Commun.*, 2013, **34**, pp. 295–298
- [6] Tallman D.E., Spinks G., Dominis A., *ET AL.*: 'Electroactive conducting polymers for corrosion control Part 1. General introduction and a review of non-ferrous metals', *J. Solid State Electrochem.*, 2002, **6**, pp. 73–84
- [7] Zarras P., Stenger-Smith J.D., Wei Y.: 'Electroactive polymers for corrosion control' (American Chemical Society, 2003)
- [8] Giglio E.D., Guascito M.R., Sabbatin L., *ET AL.*: 'Electropolymerization of pyrrole on titanium substrates for the future development of new biocompatible surfaces', *Biomaterials*, 2001, **22**, pp. 2609–2616
- [9] Srinivasan A., Ranjani P., Rajendran N.: 'Electrochemical polymerization of pyrrole over AZ31 Mg alloy for biomedical applications', *Electrochim. Acta*, 2013, **88**, pp. 310–321
- [10] Kartsonakis I.A., Balaskas A.C., Koumoulos E.P., *ET AL.*: 'Evaluation of corrosion resistance of magnesium alloy ZK10 coated with hybrid organic-inorganic film including containers', *Corros. Sci.*, 2012, **65**, pp. 481–493
- [11] Pirvu C., Mindroiu M., Stancu R., *ET AL.*: 'Scanning electronic microscopy in supporting electrochemical deposition and characterization of hybrid polymeric composite', *Key Eng. Mater.*, 2009, **415**, pp. 69–72
- [12] Yee L.M., Mahmud H.N.M.E., Kassim A., *ET AL.*: 'Polypyrrole-polyethylene glycol conducting polymer composite films: preparation and characterization', *Synth. Met.*, 2007, **157**, (8), pp. 386–389
- [13] Popescu S., Pirvu C., Mindroiu M., *ET AL.*: 'Enhancing the stability of PPy film on Ti by PEG incorporation', *Mol. Cryst. Liq. Cryst.*, 2010, **522**, (1), pp. 125–135
- [14] Pirvu C., Manole C.C., Stoian A.B., *ET AL.*: 'Understanding of electrochemical and structural changes of polypyrrole/polyethylene glycol composite films in aqueous solution', *Electrochim. Acta*, 2011, **56**, pp. 9893–9903
- [15] Yeganeh M., Saremi M.: 'Corrosion inhibition of magnesium using biocompatible Alkyd coatings incorporated by mesoporous silica nanocontainers', *Prog. Org. Coat.*, 2015, **79**, pp. 25–30
- [16] Petitjean J., Aeiya S., Lacroix J.C., *ET AL.*: 'Ultra-fast electropolymerization of pyrrole in aqueous media on oxidizable metals in a one-step process', *J. Electroanal. Chem.*, 1999, **478**, (1–2), pp. 92–100
- [17] Turhan M.C., Weiser M., Jha H., *ET AL.*: 'Optimization of electrochemical polymerization parameters of polypyrrole on Mg-Al alloy (AZ91D) electrodes and corrosion performance', *Electrochim. Acta*, 2011, **56**, pp. 5347–5354
- [18] Turhan M.C., Weiser M., Killian M.S., *ET AL.*: 'Electrochemical polymerization and characterization of polypyrrole on Mg-Al alloy (AZ91D)', *Synth. Met.*, 2011, **161**, pp. 360–364
- [19] Lyons M.E.G., Brandon M.P.: 'Show affiliations redox switching and oxygen evolution electrocatalysis in polymeric iron oxyhydroxide films', *Phys. Chem. Chem. Phys.*, 2009, **11**, (13), pp. 2203–2217
- [20] Pebere N., Riera C., Dabosi F.: 'Investigation of magnesium corrosion in aerated sodium sulfate solution by electrochemical impedance spectroscopy', *Electrochim. Acta*, 1990, **35**, (2), pp. 555–561
- [21] Zhang Y., Yan C., Wang F., *ET AL.*: 'Electrochemical behavior of anodized Mg alloy AZ91D in chloride containing aqueous solution', *Corros. Sci.*, 2005, **47**, (11), pp. 2816–2831
- [22] Lopez M.A., Pereda M.D., Valle J.A.D., *ET AL.*: 'Corrosion behaviour of AZ31 magnesium alloy with different grain sizes in simulated biological fluids', *Acta Biomater.*, 2010, **6**, (5), pp. 1763–1771
- [23] Liang C.Y., Wei Q.T., Min W.H., *ET AL.*: 'Comparison of corrosion behavior of AZ31, AZ91, AM60 and ZK60 magnesium alloys', *Trans. Nonferr. Met. Soc. China*, 2009, **19**, pp. 517–524
- [24] Turhan M.C., Lynch R., Killian M.S., *ET AL.*: 'Effect of acidic etching and fluoride treatment on corrosion performance in Mg alloy AZ91D (MgAlZn)', *Electrochim. Acta*, 2009, **55**, (1), pp. 250–257
- [25] Habashi F.: 'Kinetics of corrosion of metals', *J. Chem. Educ.*, 1965, **42**, (6), p. 318
- [26] Rongeat C., Reddy M.A., Witter R., *ET AL.*: 'Nanostructured fluorite-type fluorides as electrolytes for fluoride ion batteries', *J. Phys. Chem. C*, 2013, **117**, (10), pp. 4943–4950
- [27] Gschwind F., Kargera Z.Z., Fichtnerab M.: 'A fluoride-doped PEG matrix as an electrolyte for anion transportation in a room-temperature fluoride ion battery', *J. Mater. Chem. A*, 2014, **2**, p. 1214
- [28] Fedorková A., Náková R.O., Nák A.O., *ET AL.*: 'Electrochemical and TOF-SIMS investigations of PPy/PEG-modified LiFePO₄ composite electrodes for Li-ion batteries', *Solid State Sci.*, 2011, **13**, pp. 824–830
- [29] Schrebler R., Cury P., Gómez H., *ET AL.*: 'Electrochemical behavior of polypyrrole/polyethyleneglycol composites', *Bol. Soc. Chilena Quim.*, 2002, **47**, (4), pp. 537–545