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CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 8, Issue, 11, pp. 21449-21454, November, 2017

ISSN: 0976-3031

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

ELECTRODEPOSITION OF POLYPYRROLE ON ALUMINUM ALLOY 2024-T3 FROM DODECYLBENZENESULFONIC ACID MEDIUM

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DOI: http://dx.doi.org/10.24327/ijrsr.2017.0811.1076

ARTICLE INFO

Article History:

Received 10th August, 2017
Received in revised form 14th September, 2017
Accepted 08th October, 2017
Published online 28th November, 2017

Key Words:

Electrodeposition, Polypyrrole, Aluminum Alloy 2024-T3.

ABSTRACT

In this work polypyrrole (PPy) films were electrodeposited on aluminum alloy 2024-T3 from dodecyl benzene sulfonic acid solutions. Scanning Electron Microscopy (SEM) was used to analyze the morphology of the aluminum surfaces coated with the polymeric films. It was observed that the PPy films deposited at 0.8V were more homogeneous. Degradation of PPy takes place at high potential values as confirmed by FTIR spectrum. Furthermore, the corrosion protection of aluminum by PPy films was also investigated by open circuit potential and potentiodynamic polarization curves in chloride solution. The results indicate that the performance of polymeric films depends on the electrodeposition potential.

INTRODUCTION

Aluminum has been the choice material for aircraft construction since the 1930 due to its excellent properties as corrosion resistance, low specific mass, high electrical conductivity and good appearance [1]. However, the aluminum alloys are susceptible to pitting corrosion in chloride medium. This localized corrosion is a serious industrial problem that can be resolved using hexavalent chromium inhibitors. Although low cost and high efficiency the use of chromates compounds has been limited since 1982, due to their carcinogenic effects and environment impacts [2]. Conducting polymers represent an alternative material that has been investigated onto protection of oxidizable metals [2-4]. Polypyrrole (PPy) is an attractive material due to high conductivity, good stability and easy synthesis from aqueous or organic media by chemical and electrochemical methods [5-7].

Furthermore the properties of the PPy film can be controlled by the adjusting synthesis parameters such as current density, electrode, monomer/electrolyte concentration, electrolyte type, solvent, pH and temperature [8,9]. Various authors have studied the electrodeposition of PPy films on aluminum electrode with different electrolyte such saccharin sodium [5], tartaric acid [10], oxalate and tungstato anions [11], molibdate and nitrate [12], p-toluene sulfonic acid [13]. The studies have shown that the adherence onto metal and the performance against corrosion depend on synthesis conditions.

The literature also shows that the dopant nature influences the performance of PPy to protect the aluminum alloy. The presence of lanthanides (cerium nitrate), for example, became the PPy more efficient [14].

Researches also showed that the PPy electrodeposited in presence of vanadates, phosphates and molybdate were able to reduce the anodic dissolution of 2024 aluminum alloy [15, 16].

Hussein *et al*. have investigated the role of nanoparticles in the PPy coating and protection of aluminum. They observed that the NiLa oxide nanoparticles increased the barrier effect of the polymer layer, and they catalyzed the oxygen reduction reaction which enhances the passive state of aluminum [17].

Recently we have evaluated the performance of PPy electrodeposited from phosphoric acid medium to protect the 2024 aluminum alloy. It was observed that high potential affect the roughness and the porosity of polymeric film decreases the corrosion protection [18].

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It is important note that the electrolyte has a significant role, because can promote the metal dissolution which competes with the monomer oxidation and can difficult the polymer growth [19]. Moreover the electrolyte plays an important role in determining the porosity of the oxide film formed on electrode surface.

Although the corrosion performance of PPy films deposited in dodecyl benzene sulfonic acid (DBSA) media have been reported for stainless steel surface [20], the corrosion protection of aluminum surfaces coated with PPy films eletrodeposited in this medium has not been investigated. This work presents results of the electrodeposition of PPy films on aluminum alloy 2024-T3 in aqueous solution containing DBSA. The PPy performance to protecting the aluminum surfaces against corrosion was also studied.

Experimental

Electrochemical experiments were carried out using a Potentiostat/Galvanostat (model MQPG-01 Microquimica) in a one-compartment cell containing three electrodes: (1) working electrode - alloy aluminum 2024-T3 inlaid on Teflon® with a 0.53 cm^2 exposed area; (2) reference electrode - a saturated Ag/AgCl,Cl^- and (3) auxiliary electrode - a platinum wire. The aluminum surfaces were abraded using silicon carbide papers with different grit (320-1200 grit), washed with distilled water before each electrochemical experiment.

PPy electrodeposition was carried out by cyclic voltammetry by scanning the potential between -1.5 and 1.5 V vs. Ag/AgCl at 5.0 $mV.s^{-1}$. The PPy film growth also was performed using the potentiostatic technique by applying potential ranging between 0.8V and 1.4V vs. Ag/AgCl. The electrolytic solution was prepared by dissolving 0.1 $mol.L^{-1}$ dodecylbenzenesulfonic acid (DBSA) and 0.2 $mol.L^{-1}$ pyrrole in distilled water.

The morphology of aluminum surfaces coated with the PPy was analyzed by Scanning Electronic Microscopy (Jeol - model JXA 840A) with electron beams of 15 keV. The roughness of the aluminum surfaces coated by PPy was available by Surface Roughness Tester, model TR100.

FTIR was used to analyze the PPy films composition. The spectra were obtained using a spectrometer model SPECTRUM-2000 (Perkin Elmer). The analysis conditions were: wavenumber range of 4000-400 cm^{-1}, 4 cm^{-1} the resolution, 40 scan and ambient temperature (25°C). KBr pellets were prepared with PPy/DBSA films removed from aluminum surfaces.

The corrosion protection of aluminum surfaces by PPy films was investigated using potentialdynamic polarization curves in a 0.1 $mol.L^{-1}$ NaCl solution (pH 5.9), at 25°C. The experiments were carried out by varying the electrodes potential, at sweep rate of 1.0 $mV.s^{-1}$, from -1.5 up to +1.5V and reversing the potential down to -1.5V. The corrosion parameters were obtained from the Tafel plots.

RESULTS AND DISCUSSION

Electrodeposition of Polypyrrole

In previous works we have reported the electrodeposition of homogeneous and adherent PPy films using 0.2 $mol.L^{-1}$ electrolyte (organic acids) and 0.5 $mol.L^{-1}$ monomer. In 0.2 $mol.L^{-1}$ electrolyte, a porous aluminum oxide layer was formed, favoring the PPy film growth [21].

In this work we investigated the electrodeposition of PPy from 0.2 $mol.L^{-1}$ DBSA. Figure 1 shows the first cycle for the cyclic voltammetry performed to investigate the electrodeposition process (curve 1). It was observed that the anodic currents increase around 0.5 V which indicates the pyrrole oxidation.

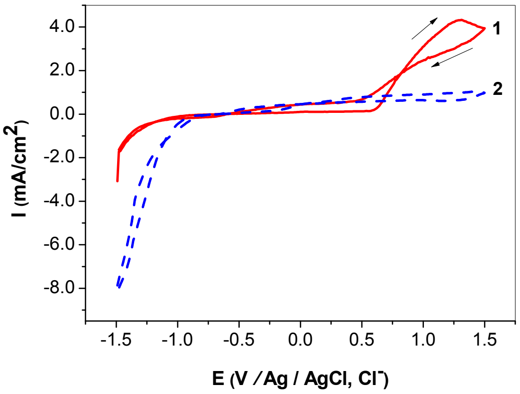


Figure 1 Cyclic voltammograms of aluminum alloy in aqueous solution of: (1) 0.1 mol L^{-1} DBSA + 0,2 $mol.L^{-1}$ pyrrole and (2) 0.1 mol L^{-1} DBSA. Scan rate: 5 mV s^{-1}

The curve 2 in Figure 1 shows the cyclic voltammetry for the aluminum electrode in monomer free solution.

The morphology of aluminum polarized in the electrolytic medium without monomer indicates the formation of a porous aluminum oxide layer that favors the PPy film growth, as confirmed by SEM (Figure 2).

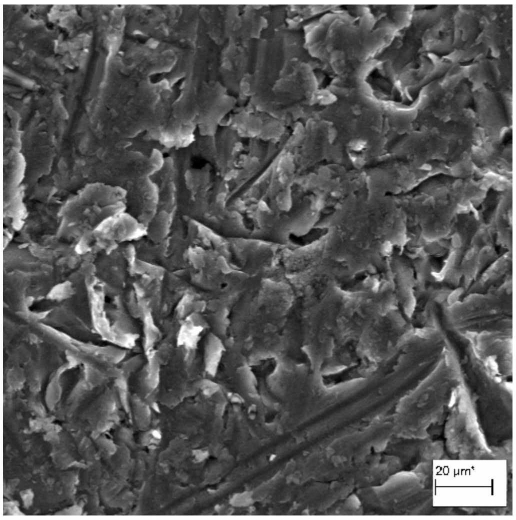


Figure 2 SEM micrograph of oxide films formed by cyclic voltammetry on aluminum exposed at DBSA aqueous solutions

Naoi *et al.* have also suggested that in the sulfonate medium occur the formation of an aluminum oxide layer with high current efficiency associated to the internal walls of the pores. The authors have also proposed that in presence of the pyrrole, the sulfonate electrolyte promotes the simultaneous formation of aluminum oxide and PPy. The pores become excellent sites to electropolymerization process [19].

The polymerization process was also performed by the potentiostatic technique. Figure 2 shows the current-time curves obtained for PPy deposition from aqueous solutions containing 0.1 mol.L^{-1} of dodecyl benzene sulfonic acid and pyrrole (0.2 mol.L^{-1}) while applying the potential between 0.8 and 1.4 V.

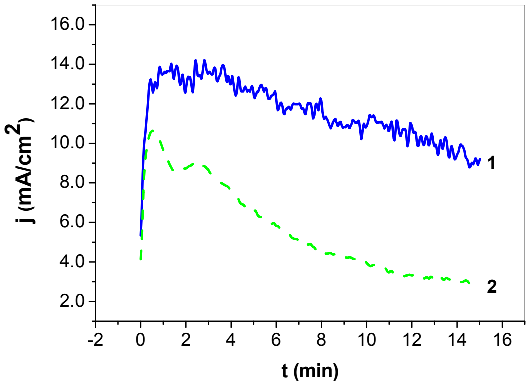


Figure 3 Current-time curves for PPy electrodeposition on aluminum from 0.2 mol.L^{-1} pyrrole and 0.1 mol.L^{-1} dodecyl benzene sulfonic acid. The applied potential was: (1) 1.4V and (2) 0.8V

Increasing the applied potential (Curve 1) the current densities shifted to higher values and increased PPy film thickness. It was noted that at higher potential the PPy coatings had low adherence onto aluminum electrode.

Applying smaller potential than 0.8V no PPy coating was formed onto aluminum electrode. This result is in accordance with that observed in cyclic voltammetry, in which the PPy growth started at 0.80V *vs*. Ag/AgCl (Curve 1 in Figure 1).

It was also observed that the currents oscillate when 1.4V was applied. This result was associated with side reactions (overoxidation) that occur in the polymer matrix at higher potentials. The Figure 4 shows the reactions that occurred during the overoxidation process [22-24].

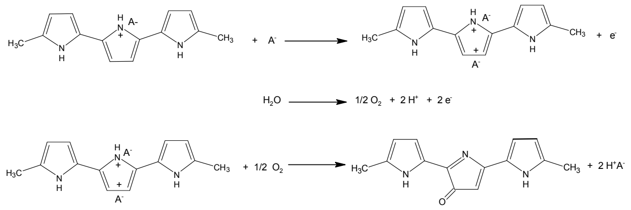


Figure 4 The overoxidation process in the polymer matrix at higher potentials

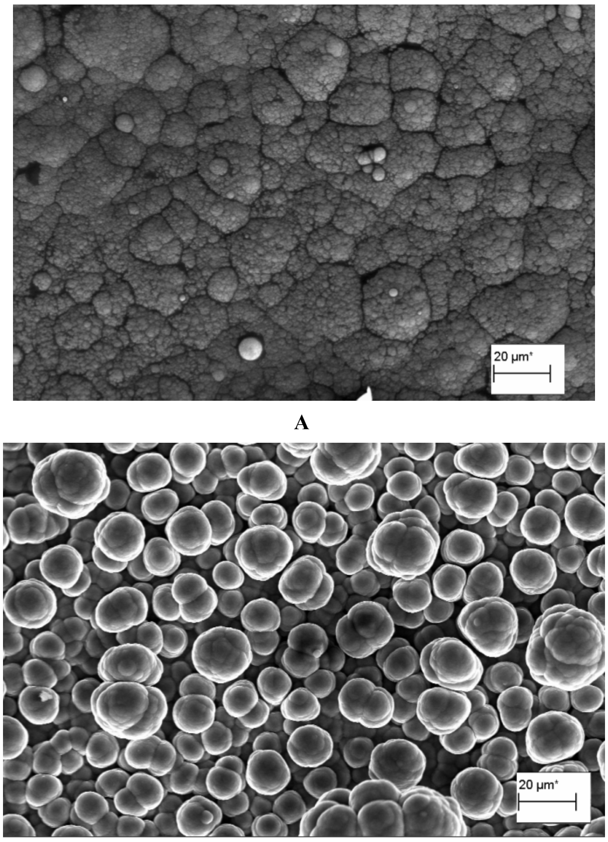
Our previous works have shown that the formation of overoxidized films onto aluminum depends on the electrolyte nature [21]. Bazzaoui *et al.* reported that the PPy electrodeposited is overoxidized in saccharin aqueous medium at potential higher than 1V *vs*. Ag/AgCl [5]. Saidman and Bessone also reported the degradation of PPy films electrodeposited in nitric acid aqueous medium takes place on aluminum at potential higher than 1.05V *vs*. SCE [25]. Furthermore, it has been reported that the doping level of PPy films decrease with increasing applied potential [26]. Decrease in the doping level with increasing applied potential may also correspond to PPy overoxidation resulting in the loss of positively charged nitrogen, accompanied by the formation of C=O species [27].

Characterization of Polypyrrole Films

Figure 5 shows the SEM micrographs of the aluminum surfaces coated by PPy films electrodeposited at 0.8V and 1.4V.

Films deposited at 0.8V were more homogeneous presenting a cauliflower-like structure constituted by micro-spherical grains. It has been reported that this cauliflower structure is related to the doping intercalation difficulty in the disordered polymeric chain [28].

It was also observed that the PPy film deposited at 0.8V is more compact than those deposited at 1.4V. This morphological difference can be explained by the overoxidation which results in defects along the PPy chain.



A

B

Figure 5 SEM of the aluminum surfaces coated with PPy films potentiostatically deposited at (A) 0.8V and (B) 1.4V

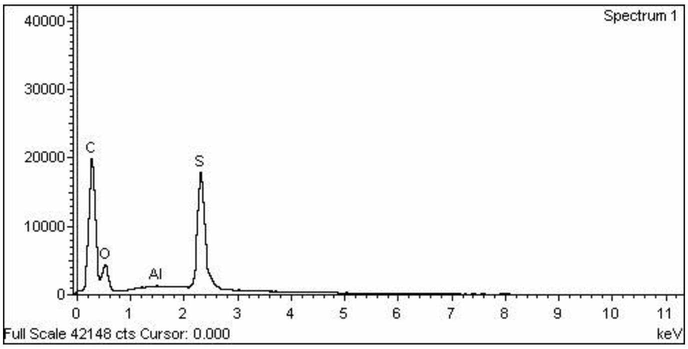


Figure 6 EDS to PPy films deposited at 0.8V.

The presence of sulfur on EDS spectrum indicates that the PPy is doped with DBSA, used as electrolyte in the electrochemical deposition.

FTIR analyses were used to investigate the composition of the PPy films removed from the aluminum surfaces. The PPy films were formed. Figure 7 shows the FTIR spectra for the films potentiostatic deposited at 0.8V and 1.4V.

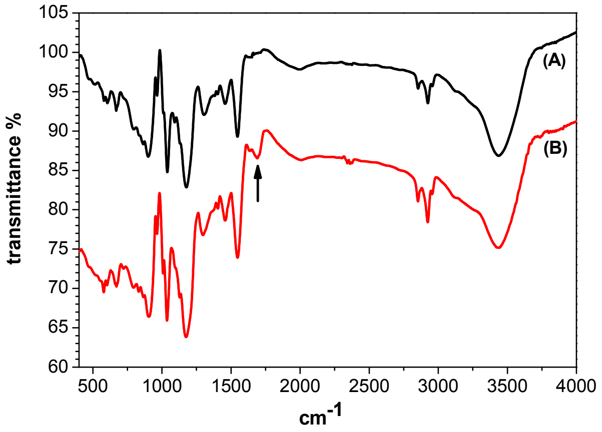


Figure 7 FTIR spectra of PPy films electrodeposited at (A) 0.8V and (B) 1.4V.

The bands at 1544 and 1455 were attributed to C-C and C-H (quinoide from polymeric chain). Furthermore the presence of the absorption bands at 1300 cm^{-1} (asymmetric axial def. O=S=O) and 1180 cm^{-1} (symmetric axial def. O=S=O) suggested that the sulfonate was incorporated into the polymer as a dopant.

The band assigned at 1686 cm^{-1} is attributed to carbonyl group formed by the overoxidation of PPy film deposited at higher potential (1.4V) [27].

Table 1 presents the values of the roughness of PPy films.

Table 1 Roughness of aluminum surfaces coated by PPy films

Surface aluminum coated by PPy	Roughness [µm]
Electrodeposited at 0.8V	1.18
Electrodeposited at 1.4V	3.96

The film deposited at 0.8V presented smaller roughness than that formed at high potentials. This result is in accordance to SEM results, which also pointed that the PPy electrodeposited at 0.8V was more compact.

Corrosion Tests

The corrosion protection of aluminum surfaces coated with PPy films was investigated in chloride medium. Figure 8 shows the potentiodynamic polarization curves in 0.1 mol L^{-1} NaCl aqueous solution to the uncoted aluminum surfaces and to those coated with PPy films synthesized under potentiostatic conditions.

The oscillations on voltammogram of uncoated electrode (curve 1) can be associated to pits formation onto uncoated aluminum alloy. It was also observed that the currents related to oxidation process were smaller to coated surfaces.

The corrosion protection afforded by PPy coatings is also presented in polarization curves (Figure 9) and the electrochemical parameters are shown in the Table 1.

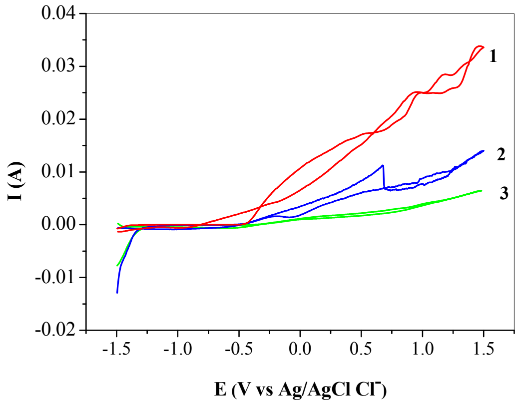


Figure 8 Cyclic voltammetry at 1.0 mV.s^{-1} in aqueous solution 0.1 mol.L^{-1} NaCl to aluminum surface: (1) uncoated and coated with PPy films at (2) 1.4V and (3) 0.8V.

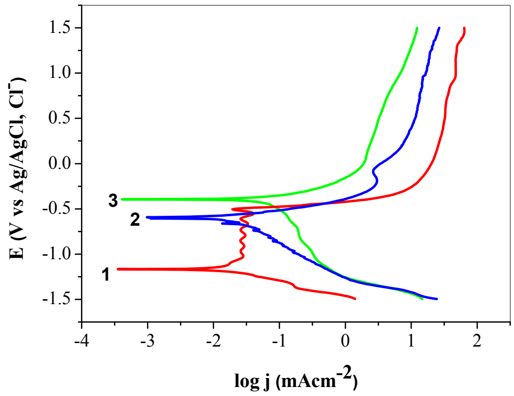


Figure 9 Polarization curves to polished aluminum surface: (1) uncoated; and coated with PPy films electrodeposited at: (2) 1.4V and (3) 0.80V.

The pitting potential for uncoated aluminum was observed at -0.48V. To aluminum coated by PPy films no pitting potential was observed in the considered potential range.

As can be seen in Figure 9, the corrosion potential of aluminum surfaces coated by polymeric films is shifted in the positive direction compared to that of the uncoated electrode indicating anodic protection [29]. Moreover the anodic current densities to coated aluminum surfaces were small than those observed to uncoated surfaces. For example, considering the potential of 0.5 V the current densities decrease in the order uncoated aluminum < aluminum/PPy 1.4V < aluminum/PPy 0.8V (Table 2).

Table 2 Corrosion parameters obtained from the Polarization curves

Aluminum Surface	$^{a}E_{corr}$ (V)	^{b}j (mA/cm^2)
Uncoated (1)	-1.16	32.36
Coated by PPy deposited at 1.4V (2)	-0.60	11.22
Coated by PPy deposited at 0.80V (3)	-0.39	3.01

^{a}Corrosion Potential, ^{b}Anodic Current Density at 0.5V

According to Table 2, the positive shift of ~0.76V in E_{corr} indicates the protection of the aluminum alloy by the polypyrrole coatings deposited at 0.8V (anodic protection) [29]. The anodic branches of the polarization curves show lower values of densities currents to aluminum surfaces coated with PPy films deposited at 1.4V. This observation can be taken as an indication that aluminum surfaces coated with PPy films are more resistant to corrosion than uncoated surfaces. However the cathodic branches show higher values of densities currents to coated surfaces. This result can be associated to the reduction reactions in the polymer chain beside the oxygen reduction.

The possible chemical reactions occurring onto aluminum surface coated with PPy during the polarizations experiments are represented bellow [30]:

Anodic Reactions
$Al \rightarrow Al^{3+} + 3\ e^{-}$
$PPy_{undoped} \rightarrow PPy_{doped} + ne^{-}$

Cathodic Reactions
$2\ H_2O + O_2 + 4\ e^{-} \rightarrow 4\ OH^{-}$
$PPy_{doped} + ne^{-} \rightarrow PPy_{undoped}$

Figure 8 shows micrograph of PPy films deposited at 0.8V after 120 h exposure in 0.1 mol.L^{-1} NaCl.

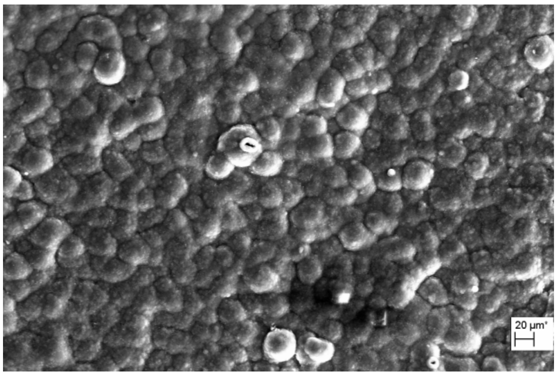


Figure 10 SEM micrograph of the Al covered with PPy/DBSA after 120 h exposure in 0.1 mol.L^{-1} NaCl

The results indicate no PPy degradation when the coated aluminum surface is immersed in an aggressive chloride medium. Furthermore no pitting was observed on metal surface after removal of polymer.

CONCLUSION

The polypyrrole synthesized in dodecyl benzene sulfonic acid solution using electrochemical process had a uniform granular morphology. It was observed that PPy film thickness increased as the increasing the applied potential. The greater porosity of PPy films eletrodeposited at 1.4 V allowed the penetration of aggressive species, thereby promoting pits formation on aluminum surfaces. The evidences showed that the mechanism of corrosion protection yet have to be fully elucidated by more studies, but is clearly that PPy coating can offers some degree of barrier protection.

Acknowledgements

This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Instituto de Pesquisa e Desenvolvimento (UNIVAP).

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How to cite this article:

Andréa Santos Liu *et al.*2017, Electrodeposition of Polypyrrole on Aluminum Alloy 2024-T3 From Dodecylbenzenesulfonic Acid Medium. *Int J Recent Sci Res.* 8(11), pp. 21449-21454. DOI: http://dx.doi.org/10.24327/ijrsr.2017.0811.1076

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