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Electrochemical deposition of conducting polymer coatings on magnesium surfaces in ionic liquid

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Abstract

A conducting polymer based smart coating for magnesium (Mg) implants that can both improve the corrosion resistance of Mg and release drug in a controllable way is reported. As the ionic liquid is a highly conductive and stable solvent with a very wide electrochemical window, the conducting polymer coatings can be directly electrodeposited on the active metal Mg in ionic liquid at mild conditions, and Mg is considerably stable during the electrodeposition. The electrodeposited Poly(3,4-ethylenedioxythiophene) (PEDOT) coatings on Mg are uniform and can significantly improve the corrosion resistance of Mg. In addition, the PEDOT coatings can load the anti-inflammatory drug dexamethasone during the electrodeposition which can be subsequently released upon electric stimulation.

Keywords

Magnesium; Conducting polymers; Electrodeposition; Ionic liquid; Controlled drug release

1. Introduction

As medical technology advances, metallic materials are being used in implantable devices to assist with tissue repair or replacement [1]. The most used metallic biomaterials are stainless steels, titanium, and cobalt-chromium based alloys. Limitations of permanent implants based on these metallic materials include the possible release of toxic metallic ions through corrosion and other potential long-term complications [2, 3]. In addition, many medical implants are only needed as temporary devices and must be removed after tissue healing. Removal requires a second surgical procedure which leads to extra cost and further patient suffering. For these applications, biodegradable materials are desired. Magnesium (Mg) has become a promising metallic material candidate for temporary implantable devices due to its attractive features, including the materials exceptionally light weight, excellent mechanical properties and ability to degrade in vivo [4]. Mg degrades by a corrosion mechanism which

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produces non-toxic products that can be harmlessly excreted in the urine [5]. Because of these desirable properties, various biodegradable Mg implants have been investigated ranging from cardiovascular stents to bone fixture devices [6, 7]. The clinical applications of Mg implants have been limited because the corrosion of pure Mg is too fast, making it difficult to control in the physiological environment. The fast Mg corrosion will result in failure of the implant, loss of mechanical integrity before the tissue has healed, and production of hydrogen gas that can cause host tissue damage [8, 9]. To tailor the corrosion rate of Mg, different strategies such as using alloying elements [9-11] and protective coatings [12] have been developed. Alloying is an effective way to control the corrosion rate, but many Mg alloys contain toxic elements that may be released to the tissue [13]. Coatings have been applied to Mg implant, including microarc oxidation coatings [14], calcium phosphate coatings [15, 16] and hydroxyapatite coatings [17, 18]. These coatings can either influence the corrosion rate, or improve biocompatibility and tissue integration of the Mg-based implants [19]. Different from the above mentioned coatings, conducting polymer coatings (CPCs) are unique as they not only have excellent anti-corrosion properties [20, 21], but can also undergo electrically controlled drug release [22, 23]. Such advantageous properties make these materials potentially useful for the development of on-demand drug release from implant surfaces to improve the host tissue responses [24, 25].

Another advantage of CPCs is that they can be evenly electrodeposited on the metal surface with ease of control over the thickness of the coatings, irrespective of the surface shape and roughness. However, the main obstacle in electrodeposition of CPCs on Mg from aqueous solution is the fast corrosion of Mg, which prevents adherent and uniform film formation on the surface. The direct electrochemical deposition of CPC on Mg has not yet been achieved, except one report that used a very severe basic condition [26]. Physical painting of blends containing conducting polymers have been used [27, 28], but the uniformity and thickness of the coatings are difficult to control. Here, we report the successful electrodeposition of CPCs, mainly poly(3,4-ethylenedioxythiophene) (PEDOT) on pure Mg in ionic liquid (IL). PEDOT is one of the most promising conducting polymers that exhibit many unique properties, such as high conductivity and great environmental stability [29]. And more importantly, PEDOT shows excellent biocompatibility [30, 31], which is essential for application in implantable devices. ILs are environmentally friendly and highly conductive solvents with very wide electrochemical windows, and they are excellent electrolytes for the electropolymerization of conducting polymers [32-34]. We show that Mg is stable in IL during the electropolymerization and uniform CPCs can be formed on Mg.

2. Materials and methods

2.1. Chemicals

Mg rods (diameter 3.2 mm, 99.9%) were purchased from Goodfellow Corporation (Oakdale, PA). 3,4-ethylenedioxythiophene (EDOT) and dexamethasone (Dex) 21-phosphate disodium salt were purchased from Sigma-Aldrich (St. Louis, MO). Pyrrole (98%) was purchased from Sigma-Aldrich, vacuum distilled and stored frozen. The IL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (electrochemical grade, > 99.5% purity) was purchased from Covalent Associates, Inc. (Corvallis, OR). Phosphate buffered saline (PBS, pH 7.4) was purchased from Sigma-Aldrich, and the used PBS contain 10 mM sodium phosphate and 0.9% NaCl. All other chemicals were of analytical grade, and Milli-Q water from a Millipore Q water purification system was used throughout.

2.2. Apparatus

Electrochemical experiments were performed using a Gamry Potentiostat, FAS2/FemtoStat (Gamry Instruments) with Gamry Framework software. For polarization and electrical drug

release, conventional three-electrode system was used, with the Mg rod as the working electrode, a platinum coil as the counter electrode, and a silver/silver chloride (Ag/AgCl) as the reference electrode (CH Instruments). For the electrodeposition of CPCs on Mg in IL, a Pt wire was used as a pseudo-reference electrode. The Pt pseudo-reference electrode was determined to be +337 mV versus the Ag/AgCl reference electrode by measuring cyclic voltammetry (CV) of 0.1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis were performed with an XL30 SEM instrument (FEI Company). The concentration of Dex solution was measured with a SpectraMax M5 (Molecular Devices) microplate reader, using ultraviolet (UV) absorption of Dex at 242 nm. The polarization experiment was carried out in PBS by scanning at a rate of 2 mV/s. The corrosion potential and current were determined using the Gamry DC Corrosion Techniques Software DC 105.

2.3. Preparation of Mg electrodes

Mg rods were firstly polished with sand paper and washed with 1.0 M HCl for 2~3 seconds, and followed by rinsing with water and ethanol to remove the surface impurities and oxide layer. Secondly, the clean and dried Mg rods were dip-coated with the solution of 10% (w/w) polystyrene (PS) in toluene on one end, and they were dried at 60 °C in an oven for one hour. After the evaporation of toluene, a thin layer of PS was formed on the Mg rods. The dip-coating process was repeated three times to obtain suitable PS coatings on Mg rods. Finally, the PS coated tips of the Mg rods were cut with a knife to remove the PS layer, and the exposed Mg tips were polished with 1.0, 0.3 and 0.05 μm alumina slurries in sequence and then ultrasonically washed in water and ethanol for about 5 min, respectively. Therefore, Mg rods with smooth tips exposed will have defined active surface area, and they will be used as electrodes for further studies.

2.4. Electrodeposition of conducting polymer coatings on Mg

For the electrodeposition of PEDOT coatings on Mg, the electrodeposition solution was pure IL containing 0.2 M EDOT. For the chronoamperometric deposition, a constant potential of 1.2 V (vs. Pt wire) was applied for 200s; while for the cyclic voltammetric (CV) deposition, the potential was scanned from -0.5 to 2.0 V (vs. Pt wire) at a scan rate of 100 mV/s for 10 cycles, if not otherwise stated. The solution for the electrodeposition of polypyrrole (PPy) was pure IL containing 0.4 M pyrrole. For the chronoamperometric deposition of PPy, a constant potential of 1.2 V (vs. Pt wire) was applied for one hour; while for the CV deposition, the potential was scanned from -2.0 to 2.0 V (vs. Pt wire) at a scan rate of 100 mV/s for 30 cycles, if not otherwise stated. For the electrodeposition of PEDOT coatings loaded with Dex on Mg, the same method was applied, but the electrodeposition solution was pure IL containing 0.2 M EDOT and 5.0 mg/mL Dex.

2.5. Electrically controlled drug release

After electrodeposition, the PEDOT coatings on Mg with and without Dex were thoroughly washed with water to remove the adsorbed Dex. The electrically controlled release of drug from the coatings was carried out in a small electrochemical cell containing 2.0 mL 10 mM PBS (pH 7.4). The electrical stimulation applied for drug release was - 2.0 V (vs. Ag/AgCl) for 20 s each time. All the diffusion tests were performed by dipping the coated or uncoated electrodes in 10 mM PBS (pH 7.4) for 100s. The solution with the released drug was sampled and transferred to a 96 well Costar clear assay plate and analyzed using UV absorption measurement at 242 nm. All the obtained drug release data were based on three measurements.

3. Results and discussion

Critical for the quality of the CPCs electrodeposited on active metal is the stability of the substrate in the electrolyte. To test the stability of Mg in IL, the Mg electrode was soaked in the IL with an applied potential of 1.2 V for 1 h. After this treatment, the Mg rod surface was characterized with SEM and EDX analysis (data not shown), and there was no significant change in the morphology or elemental composition. The electrochemical impedance and polarization characterizations of the Mg also did not show any significant changes after this treatment. These findings indicate that Mg did not corrode significantly after soaking in the IL, even under an applied anodic potential, an observation similar to a previous report [35]. It was reported that Mg and its alloy may slowly react with ILs, and form a thin corrosion resistive barrier film over hours [36, 37]. Such a film was not observed on Mg after the treatment for one hour described above maybe because in this case the oxide layer is too thin. Most importantly, it did not prevent the electrodeposition of CPCs on Mg.

PEDOT is a conducting polymer that has been investigated in many biomedical applications [30, 38]. The electropolymerization of PEDOT in IL on inert conductive substrates, such as SnO_2 [39], gold [40] and glassy carbon [41] has been reported. To test whether PEDOT can be electrodeposited on the very active metal substrate of Mg in IL, two electrochemical techniques, chronoamperometry and CV were used for electrodeposition. For the chronoamperometric deposition, PEDOT can be deposited on Mg in the IL within the potential range of 1.0 to 1.4 V. At the optimized potential of 1.2 V, uniform and adhesive PEDOT coatings on Mg surfaces can be obtained, as shown in Figure 1a. The fine structure of the PEDOT coating was revealed using SEM at a higher magnification (Figure 1b), and the coating showed a porous morphology consisted of branched and connected particles. This morphology of PEDOT coating is different from that of PEDOT films grown on SnO_2 substrate in IL, where the films showed microstructures of randomly oriented nanofibers and particles [39].

A typical EDX spectrum of a PEDOT coating electrodeposited on Mg is shown in Figure 1d, which shows strong signals from C, O, F and S, and weak signals from N and Mg. As the pure PEDOT backbone will only give the signals for C, O and S, the elemental F and N signals must come from the IL. It is known that during the electropolymerization of conducting polymer monomers in ILs, the anions of the ILs will act as the dopants or counter ions for the synthesized conducting polymers [32, 42]. Here the anion of the IL is $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, and its presence in the polymer film is confirmed by the EDX signature of F and N.

The PEDOT coatings can also be electrodeposited on Mg in IL using CV, as shown in Figure 2. Macroscopically, the morphology of the PEDOT coating is similar to that electrodeposited at a constant potential, but less uniform. When visualized under SEM, the microstructure of this coating (Figure 2b) appeared dense and nodular. The CV curves of PEDOT synthesis in IL on Mg is shown in Figure 2c. Unlike the synthesis curves of normal conducting polymer on noble metal electrodes, the redox peaks are not well defined and the separation of the peaks is large, which might either be due to the high viscosity of the IL or to an interface resistance between PEDOT and the possible oxide layer of magnesium. However, there is a general trend of peak current increase as the deposited film thickens, which is typical of electroactive conducting polymer films.

The electrodeposition of another commonly studied conducting polymer, PPy on Mg in IL was also investigated. According to the SEM and EDX analysis (Figure 3), it is clear that PPy coatings can be electrodeposited on Mg in IL, using both chronoamperometric and CV methods, and the coatings are composed of PPy polymer backbones doped with the anions

of the IL. However, compared to PEDOT, the electrodeposition of PPy is more difficult, and the coating is less uniform and can easily detach from the Mg surface.

These electrodeposition results demonstrate that by using IL, various CPCs can be electropolymerized on Mg substrate, which was previously a technical challenge. When coating CPCs onto real Mg implantable devices which may possess irregular geometries of different scales, the uniformity of the electrodeposited coatings may be affected due to the variations in electric field strengths in the electrochemical system. This effect may be minimized by using properly shaped counter electrodes or slowly rotating the devices during electrodeposition. In the case of devices with extremely complex shape, other means of coating like chemical polymerization of conducting polymers may be better suited.

The PEDOT coatings are further characterized for possible applications in anti-corrosion. Figure 4 shows the polarization curves of the bare Mg and PEDOT coated Mg. In contrast to the bare Mg, the corrosion potential of the PEDOT coated Mg was increased by about 120 mV, and the corrosion current of the PEDOT coated Mg was decreased by about 50%. These indicate that the corrosion resistance of Mg has been improved by the PEDOT coating. Although the PEDOT coatings cannot prevent the Mg from corrosion completely, it can slow down the corrosion rate of Mg to some degree by lowering the corrosion potential of Mg, and this is potentially useful for degradable Mg implants. In the future, we will try to optimize the PEDOT coating for Mg (or less active Mg alloy), and investigate the effect of the coating on the lifetime of the Mg or Mg alloy to see if this can be tuned.

Another potential application of the PEDOT coating on Mg is the electrically controlled drug release, which may mitigate the inflammatory tissue response to Mg implants by locally delivering anti-inflammatory drugs, such as Dex. To load the drug, the phosphate salt form of Dex (5.0 mg/ml) was added to the EDOT IL solution. During the electrodeposition of PEDOT on Mg in IL, the anionic Dex was incorporated in the PEDOT coating as dopant, competing with the anions of IL. After thorough wash with water, the PEDOT coating is soaked in electrolyte solution and the release of drug via diffusion was found to be negligible (Figure 5a). Upon applied potential of -2V for 20 seconds, an average of about 16.3 μ g Dex was released from the PEDOT coatings with Dex (PEDOT/IL/Dex), while there was no significant drug release in the control electrodes (bare Mg and Mg coated with PEDOT/IL film without Dex), as shown in Figure 5a.

When the PEDOT coating loaded with Dex was electrically stimulated (applied potential of -2V for 20 seconds each time) multiple times, successive drug release was detected, as shown in Figure 5b. This confirms that the Dex added to the electrodeposition solution was loaded in the PEDOT coatings, and the loaded drug can be electrically released in a controllable way. Since the drug release was carried out in PBS, which can cause the corrosion of Mg gradually, in some cases, the PEDOT coatings may partly detach from the Mg surface after multiple stimulations. This would not be a problem when less active substrates (like Mg alloy) are used. It should be pointed out that the drug release stimulus may also cause the anion of ionic liquid to be released, and in vivo applications would need to use biocompatible ILs that have been proven to be nontoxic [43, 44].

Although PEDOT was reported to be biocompatible in many studies [30, 31], its mode of degradation *in vivo* is not yet known. Therefore, rigorous long-term *in vivo* biocompatibility and biodegradability studies of PEDOT need to be completed in the future. If necessary, PEDOT can be chemically modified to become biodegradable by introducing hydrolyzable linkage groups or segments in the backbone [45].

4. Conclusion

CPCs can be electrodeposited on the surface of Mg, while the Mg itself remains stable during the electrodeposition process. The synthesized PEDOT coatings on Mg are uniform and can improve the corrosion resistance of Mg. Moreover, drug molecules can be loaded in the PEDOT coatings on Mg during their electrodeposition in IL, and the loaded drugs can be subsequently released upon electric stimulation. It is expected that the proposed CPCs could be electrodeposited on other active metals and alloys besides pure Mg, and such CPCs with drug releasing properties may find applications in Mg based implantable devices.

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References

1. Niinomi M. Recent metallic materials for biomedical applications. *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science*. 2002; 33:477–86.
2. Erne P, Schier M, Resink TJ. The road to bioabsorbable stents: Reaching clinical reality? *Cardiovascular and Interventional Radiology*. 2006; 29:11–16. [PubMed: 16195840]
3. Colombo A, Karvouni E. Biodegradable stents - “Fulfilling the mission and stepping away”. *Circulation*. 2000; 102:371–73. [PubMed: 10908206]
4. Staiger MP, Pietak AM, Huadmai J, Dias G. Magnesium and its alloys as orthopedic biomaterials: A review. *Biomaterials*. 2006; 27:1728–34. [PubMed: 16246414]
5. Saris NEL, Mervaala E, Karppanen H, Khawaja JA, Lewenstam A. Magnesium - An update on physiological, clinical and analytical aspects. *Clinica Chimica Acta*. 2000; 294:1–26.
6. Peuster M, Hoehn R, Hesse C, Drynda A. Development and evaluation of newer, biodegradable stents and magnesium-base in peripheral design. *Clinical Research in Cardiology*. 2008; 97:683–83.
7. Witte F, Ulrich H, Palm C, Willbold E. Biodegradable magnesium scaffolds: Part II: Peri-implant bone remodeling. *Journal of Biomedical Materials Research Part A*. 2007; 81A:757–65. [PubMed: 17390322]
8. Witte F, Kaese V, Haferkamp H, Switzer E, Meyer-Lindenberg A, Wirth CJ, Windhagen H. In vivo corrosion of four magnesium alloys and the associated bone response. *Biomaterials*. 2005; 26:3557–63. [PubMed: 15621246]
9. Zberg B, Uggowitzer PJ, Löffler JF. MgZnCa glasses without clinically observable hydrogen evolution for biodegradable implants. *Nature Materials*. 2009; 8:887–91.
10. Heublein B, Rohde R, Kaese V, Niemeyer M, Hartung W, Haverich A. Biocorrosion of magnesium alloys: a new principle in cardiovascular implant technology? *Heart*. 2003; 89:651–56. [PubMed: 12748224]
11. Peeters P, Bosiers M, Verbist J, Deloose K, Heublein B. Preliminary results after application of absorbable metal stents in patients with critical limb ischemia. *Journal of Endovascular Therapy*. 2005; 12:1–5. [PubMed: 15683259]
12. Gray JE, Luan B. Protective coatings on magnesium and its alloys - a critical review. *Journal of Alloys and Compounds*. 2002; 336:88–113.
13. Witte F, Hort N, Vogt C, Cohen S, Kainer KU, Willumeit R, Feyerabend F. Degradable biomaterials based on magnesium corrosion. *Current Opinion in Solid State & Materials Science*. 2008; 12:63–72.
14. Wang YM, Wang FH, Xu MJ, Zhao B, Guo LX, Ouyang JH. Microstructure and corrosion behavior of coated AZ91 alloy by microarc oxidation for biomedical application. *Applied Surface Science*. 2009; 255:9124–31.

15. Gray-Munro JE, Strong M. The mechanism of deposition of calcium phosphate coatings from solution onto magnesium alloy AZ31. *Journal of Biomedical Materials Research Part A*. 2009; 90A:339–50. [PubMed: 18508354]
16. Yang JX, Cui FZ, Yin QS, Zhang Y, Zhang T, Wang XM. Characterization and Degradation Study of Calcium Phosphate Coating on Magnesium Alloy Bone Implant In Vitro. *Ieee Transactions on Plasma Science*. 2009; 37:1161–68.
17. Wen CL, Guan SK, Peng L, Ren CX, Wang X, Hu ZH. Characterization and degradation behavior of AZ31 alloy surface modified by bone-like hydroxyapatite for implant applications. *Applied Surface Science*. 2009; 255:6433–38.
18. Song YW, Shan DY, Han EH. Electrodeposition of hydroxyapatite coating on AZ91D magnesium alloy for biomaterial application. *Materials Letters*. 2008; 62:3276–79.
19. Li LC, Gao JC, Wang Y. Evaluation of cyto-toxicity and corrosion behavior of alkali-heat-treated magnesium in simulated body fluid. *Surface & Coatings Technology*. 2004; 185:92–98.
20. Sitaram SP, Stoffer JO, OKeefe TJ. Application of conducting polymers in corrosion protection. *Journal of Coatings Technology*. 1997; 69:65.
21. Tallman DE, Spinks G, Dominis A, Wallace GG. Electroactive conducting polymers for corrosion control Part 1. General introduction and a review of non-ferrous metals. *Journal of Solid State Electrochemistry*. 2002; 6:73–84.
22. Wadhwa R, Lagenaur CF, Cui XT. Electrochemically controlled release of dexamethasone from conducting polymer polypyrrole coated electrode. *Journal of Controlled Release*. 2006; 110:531–41. [PubMed: 16360955]
23. Abidian MR, Kim DH, Martin DC. Conducting-polymer nanotubes for controlled drug release. *Advanced Materials*. 2006; 18:405. [PubMed: 21552389]
24. Anis RR, Karsch KR. The future of drug eluting stents. *Heart*. 2006; 92:585–88. [PubMed: 16216857]
25. Kukreja N, Onuma Y, Daemen J, Serruys PW. The future of drug-eluting stents. *Pharmacological Research*. 2008; 57:171–80. [PubMed: 18339557]
26. Guo XW, Jiang YF, Zhai CQ, Lu C, Ding WJ. Preparation of even polyaniline film on magnesium alloy by pulse potentiostatic method. *Synthetic Metals*. 2003; 135:169–70.
27. Truong VT, Lai PK, Moore BT, Muscat RF, Russo MS. Corrosion protection of magnesium by electroactive polypyrrole/paint coatings. *Synthetic Metals*. 2000; 110:7–15.
28. Sathiyarayanan S, Azim SS, Venkatachari G. Corrosion protection of magnesium alloy ZM21 by polyaniline-blended coatings. *Journal of Coatings Technology and Research*. 2008; 5:471–77.
29. Groenendaal BL, Jonas F, Freitag D, Pielartzik H, Reynolds JR. Poly(3,4-ethylenedioxythiophene) and its derivatives: Past, present, and future. *Advanced Materials*. 2000; 12:481–94.
30. Luo SC, Ali EM, Tansil NC, Yu HH, Gao S, Kantchev EAB, Ying JY. Poly(3,4-ethylenedioxythiophene) (PEDOT) nanobiointerfaces: Thin, ultrasmooth, and functionalized PEDOT films with in vitro and in vivo biocompatibility. *Langmuir*. 2008; 24:8071–77. [PubMed: 18588322]
31. Richardson-Burns SM, Hendricks JL, Foster B, Povlich LK, Kim DH, Martin DC. Polymerization of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) around living neural cells. *Biomaterials*. 2007; 28:1539–52. [PubMed: 17169420]
32. Hapiot P, Lagrost C. Electrochemical reactivity in room-temperature ionic liquids. *Chemical Reviews*. 2008; 108:2238–64. [PubMed: 18564878]
33. Pringle JM, Forsyth M, Wallace GG, MacFarlane DR. Solution-surface electropolymerization: A route to morphologically novel poly(pyrrole) using an ionic liquid. *Macromolecules*. 2006; 39:7193–95.
34. Schneider O, Bund A, Ispas A, Borissenko N, El Abedin SZ, Endres F. An EQCM study of the electropolymerization of benzene in an ionic liquid and ion exchange characteristics of the resulting polymer film. *Journal of Physical Chemistry B*. 2005; 109:7159–68.
35. Shkurankov A, El Abedin SZ, Endres F. AFM-assisted investigation of the corrosion behaviour of magnesium and AZ91 alloys in an ionic liquid with varying water content. *Australian Journal of Chemistry*. 2007; 60:35–42.

36. Forsyth M, Neil WC, Howlett PC, Macfarlane DR, Hinton BRW, Rocher N, Kemp TF, Smith ME. New Insights into the Fundamental Chemical Nature of Ionic Liquid Film Formation on Magnesium Alloy Surfaces. *Acs Applied Materials & Interfaces*. 2009; 1:1045–52. [PubMed: 20355890]
37. Birbilis N, Howlett PC, MacFarlane DR, Forsyth M. Exploring corrosion protection of Mg via ionic liquid pretreatment. *Surface & Coatings Technology*. 2007; 201:4496–504.
38. Rozlosnik N. New directions in medical biosensors employing poly(3,4-ethylenedioxy thiophene) derivative-based electrodes. *Analytical and Bioanalytical Chemistry*. 2009; 395:637–45. [PubMed: 19644677]
39. Ahmad S, Deepa M, Singh S. Electrochemical synthesis and surface characterization of poly(3,4-ethylenedioxythiophene) films grown in an ionic liquid. *Langmuir*. 2007; 23:11430–33. [PubMed: 17915903]
40. Snook GA, Best AS. Co-deposition of conducting polymers in a room temperature ionic liquid. *Journal of Materials Chemistry*. 2009; 19:4248–54.
41. Danielsson P, Bobacka J, Ivaska A. Electrochemical synthesis and characterization of poly(3,4-ethylenedioxythiophene) in ionic liquids with bulky organic anions. *Journal of Solid State Electrochemistry*. 2004; 8:809–17.
42. Macfarlane DR, Forsyth M, Howlett PC, Pringle JM, Sun J, Annat G, Neil W, Izgorodina EI. Ionic liquids in electrochemical devices and processes: managing interfacial Electrochemistry. *Accounts of Chemical Research*. 2007; 40:1165–73. [PubMed: 17941700]
43. Weaver KD, Kim HJ, Sun JZ, MacFarlane DR, Elliott GD. Cyto-toxicity and biocompatibility of a family of choline phosphate ionic liquids designed for pharmaceutical applications. *Green Chemistry*. 2010; 12:507–13.
44. Petkovic M, Ferguson JL, Gunaratne HQN, Ferreira R, Leitao MC, Seddon KR, Rebelo LPN, Pereira CS. Novel biocompatible cholinium-based ionic liquids-toxicity and biodegradability. *Green Chemistry*. 2010; 12:643–49.
45. Guimard NKE, Sessler JL, Schmidt CE. Toward a Biocompatible and Biodegradable Copolymer Incorporating Electroactive Oligothiophene Units. *Macromolecules*. 2009; 42:502–11. [PubMed: 20046223]

Figure 1. SEM (a, b) and EDX (d) analysis of PEDOT/IL coating electrodeposited on Mg using chronoamperometry. The electrodeposition of PEDOT was carried out in IL solution containing 0.2 M EDOT, with an applied potential of 1.2 V for 200 s. Figure (c) is the EDX spectrum of bare Mg.

Figure 2. SEM images (a, b) of PEDOT/IL coating electrodeposited on Mg using cyclic voltammetry and the selected CV curves (c) during synthesis.

Figure 3. SEM (a, b) and EDX (c, d) analysis of PPy/IL coatings electrodeposited on Mg using cyclic voltammetry (a, c) and chronoamperometry (b and d, the coating characterized is detached from Mg).

Figure 4. Polarization curves of bare Mg and Mg covered with PEDOT coating in 10 mM pH 7.4 PBS.

Figure 5. (a) Electrically controlled drug release from different systems in comparison to diffusion. PEDOT/IL/Dex/Mg, PEDOT coating with Dex electrodeposited on Mg; PEDOT/IL/Mg, PEDOT coating without Dex electrodeposited on Mg; Mg, bare Mg electrode. (b) Accumulated drug release of the PEDOT/IL/Dex/Mg upon multiple electrical stimulation. The error bar represents the standard error of the mean ($n = 6$).