# A MEMS-ENABLED BIODEGRADABLE BATTERY FOR POWERING TRANSIENT IMPLANTABLE DEVICES

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# ABSTRACT

Active implantable medical devices (IMD) for the monitoring and treatment of transient disease states have garnered increasing interest in the medical research community. In order for these technologies to be fully viable, they require a similarly biodegradable energy source. This study presents a series of MEMS-enabled biodegradable batteries comprising Mg anodes and Fe cathodes in a 0.1 M MgCl<sub>2</sub> electrolyte. The anode was fabricated bv electroplating Mg from a non-aqueous solution and passivated with either polycaprolactone or poly(glycerol-sebacate). Mg anodes coated with the biodegradable polymers hindered parasitic corrosion of the biodegradable anode and significantly enhanced the performance of the battery. The batteries demonstrated a capacity and power delivery capability of up to 0.7 mAh and 26 µW, respectively, which are sufficient for powering MEMS-based IMD systems.

# **INTRODUCTION**

Recent developments in biodegradable electronics offer new challenges in the field of energy sources. Implantable medical devices (IMDs) for the monitoring and treatment of transient diseases, such as bone fracture or wound healing and drug delivery systems, have typically been limited to either passive designs or wireless powering [1]. The development of biodegradable batteries, however, would support this emerging technology by providing an alternative means to power active transient devices. The ideal power source for transient IMDs should be biocompatible, and comprise biodegradable chemistries that would satisfy device power requirements during the lifetime of the IMD and benignly degrade thereafter. For reference, the power consumption of currently available non-degradable IMDs ranges from 10-1000 µW [2].

Magnesium (Mg), iron (Fe) and zinc (Zn) are metals that may be considered for biodegradable battery chemistries [3]. These metals have already found applications in biodegradable implants, such as stents and bone screws, with demonstrated biocompatibility in vivo [4]. In particular, Mg offers desirable mechanical and electrochemical properties. Magnesium is a light, alkaline earth metal with a density of  $1.74 \text{ g/cm}^3$ , comparable to that of aluminum. Magnesium also features a standard electrode potential of -2.34 V vs. standard hydrogen electrode (SHE) and a theoretical capacity of 2.2 Ah/g. Magnesium films at thicknesses greater than

1 µm can be micropatterned by the subtractive etching of commercial Mg foil or electrodeposited from a non-aqueous solution [5]. Similarly, Fe films can be fabricated by physical vapor deposition and aqueous electrodeposition.

This study presents the design, fabrication and testing of a biodegradable Mg/Fe battery for the powering of transient IMDs. The battery features a Mg anode and Fe cathode in a 0.1 M magnesium chloride (MgCl<sub>2</sub>) electrolyte solution. The governing chemistry of the battery is the cathodic protection of the Fe electrode through the oxidation of Mg and, thus, reduction of hydrogen on the Fe cathode surface (Figure 1). In addition to these discharge reactions, Mg naturally degrades in aqueous solutions. This effect, or parasitic corrosion of the Mg, would detract from the capacity and energy of the battery. To hinder this effect, the Mg surface was protected with either polycaprolactone (PCL) or poly(glycerol-sebacate) (PGS), both biodegradable and biocompatible polymers [6]. As the thickness and permeability of the polymeric coating may contribute to mass transfer resistance and impact discharge performance of the battery, PCL and PGS were compared at varying thicknesses to determine the relevant parameters for achieving a high coulombic efficiency and discharge potential. The timescale of PCL and PGS degradation (i.e., months) exceeds the lifetime of the battery, and the thickness of the polymer coating does not appreciably change during discharge of the battery. The electrolyte was selected as MgCl<sub>2</sub> because Mg<sup>2+</sup> and Cl<sup>-</sup> ions are constituents of physiological solutions [7].



Figure 1: Schematic of the Mg/Fe biodegradable battery. *Electrolyte diffuses across the polymer coating and native* magnesium hydroxide  $(Mg(OH)_2)$  film to reach the Mg surface, where oxidation reactions that supply electrons for the battery and generate hydrogen occur. The  $Mg(OH)_2$ formation is countered by mechanical disruption of this passive film from the discharge current. Hydrogen is reduced on the Fe cathode surface.

In this initial study, a silicon battery substrate and acrylic electrolyte cell were used to isolate any effects of biodegradable packaging. The longer-term goals are to implement biodegradable packaging and substrate for these batteries as well.

## EXPERIMENTAL

## Fabrication of the Mg/Fe battery

Fabrication of the biodegradable battery began with through-mold electrodeposition of Mg to form the anode (Figure 2). Silicon dioxide (500 µm thickness) and metallic seed layers (50 nm Ti/ 500 nm Cu/ 50 nm Ti) were deposited onto a silicon wafer by plasma-enhanced chemical vapor deposition (PECVD) and sputter deposition, respectively. To achieve a mesh seed layer, the Ti and Cu were chemically etched through a photomask. Next, an electroplating mold was patterned using polyvinyl alcohol (PVA). a water-soluble polymer with low solubility in solvent solutions. The negative image of the electroplating mold was patterned with NR-21 photoresist (Futurrex), and PVA (33 w/v%) was spin-coated onto the wafer and cured. A brief oxygen plasma treatment removed any PVA coating the edges of the photoresist. The sample was sonicated in acetone to achieve a micropatterned water-soluble mold.

Magnesium was electroplated from a non-aqueous solution of methylmagnesium chloride and aluminum chloride at a 6:1 molar ratio in tetrahydrofuran (THF). The electrodeposition was performed in a moisture-free glove box under inert nitrogen atmosphere. Pulse plating was conducted with an average current density of 10 mA/cm<sup>2</sup> at 20% duty cycle to a thickness of 35  $\mu$ m. The electroplating mold was removed by solubilizing in water. The Mg anode was coated with either PCL or PGS. Commercial 80 kDa PCL pellets were solubilized in trifluoroethanol at a concentration of 100 mg/mL. PGS was synthesized by a polycondensation reaction of sebacic acid and glycerol, as described in [6], and diluted in THF (33 w/v%). PCL or PGS



Figure 2: (a) Fabrication process and (b) testing setup of the Mg/Fe battery, and (c) optical and (d) SEM images of the electroplated Mg anode.

was spin-coated onto the Mg anode at varying thicknesses, and cured at room temperature and at 120°C under vacuum, respectively.

The Fe cathode was patterned by e-beam evaporation through a Kapton (DuPont) shadow mask to a thickness of 300 nm. Both the shadow mask and electrolyte cell were fabricated by laser micromachining with a  $CO_2$  laser.

#### Characterization of battery components

The surface morphology and elemental composition of the Mg and Fe electrodes were characterized by SEM/EDX (Hitachi S-3700N). Potentiodynamic polarization tests were performed between -1.7 and -1.2 V at a scan rate of 1 mV/s to characterize the corrosion behavior of electroplated Mg and the effect of polymeric coatings. A three-electrode setup was implemented with Mg, Pt, and Ag/AgCl as the working, counter, and reference electrodes, respectively. Tests were conducted in 0.1 M aqueous MgCl<sub>2</sub> solution with a potentiostat (Wavedriver 10, Pine Instruments).

Water vapor permeability tests were performed to evaluate the barrier properties of the biodegradable polymers. Glass vials filled with calcium oxide, a hygroscopic desiccant, were fitted with polyethylene filter connectors containing either PCL or PGS membranes. The polymer membranes were 400  $\mu$ m in thickness and cut with a CO<sub>2</sub> laser. The filters were filled with 1 mL of DI water to provide saturated conditions on one side of the polymer membrane and sink conditions within the vial. Silicone o-rings were used to provide a tight seal and the system was wrapped in parafilm. At periodic time points, the glass vials were removed and weighed to determine the rate of water permeation across the polymers.

#### Electrochemical testing of biodegradable batteries

A two-electrode-cell configuration, where Mg and Fe serve as anode and cathode, respectively, was utilized to test the performance of the batteries with a potentiostat (Model 263, EG&G Princeton Applied Research). The electrolyte was selected as 0.1 M aqueous MgCl<sub>2</sub> solution, which provided a conductivity of 0.9 mS/cm. Tests were performed under galvanostatic conditions at a discharge current of 25  $\mu$ A.

#### **RESULTS & DISCUSSION**

#### Characterization of battery components

Figure 2 shows optical and SEM images of the microfabricated Mg anode. Surface elemental analysis confirmed the atomic composition of the electroplated metal as 95% Mg and 5% O (data not shown). While the theoretical standard electrode potential of Mg is -2.34 V, this value is not observed in practice due to a native Mg(OH)<sub>2</sub> film that forms on the Mg surface. Electrolyte must first diffuse across the passive film to react with the Mg. The film is further disrupted mechanically during current draw to expose more active material to the electrolyte [8]. Figure 3 shows the polarization curves of uncoated Mg and Mg coated with either PCL or PGS in the proposed electrolyte. Uncoated Mg demonstrated a corrosion potential of -1.32 V vs. SHE. This



Figure 3: Polarization curves of the Mg anode coated with PCL and PGS at varying thicknesses, compared against uncoated Mg, in a 0.1M MgCl<sub>2</sub>.



Figure 4: Water vapor permeability of PCL and PGS membranes (400  $\mu$ m thickness). Data are mean <u>+</u> SEM; n=3.

is in agreement with literature values for Mg in dilute chloride solutions [9]. In contrast, Mg coated with 15  $\mu$ m of PCL or PGS exhibited corrosion potentials of -1.292 V and -1.165 V, respectively. The corrosion potential shifted towards the noble direction with PCL and PGS coatings, suggesting that the polymer coatings reduced the parasitic corrosion of Mg in the electrolyte solution [9-10]. The higher corrosion potentials observed with PGS coatings that PCL coatings further suggested that Mg coated with PGS may be more corrosion resistant. The fluctuations observed in the anodic curves were attributed to the pitting nature of Mg corrosion, with repeated breakdown and formation of the passivating film [9].

As a first step towards understanding ion transport across the biodegradable polymers, water permeability tests were conducted to evaluate the diffusion properties of the polymers (Figure 4). As shown in Figure 4, the rate of water transport across the PCL and PGS membranes were  $0.08 \text{ mg/cm}^2/\text{h}$  and  $0.19 \text{ mg/cm}^2/\text{h}$ , respectively. These findings confirmed that the polymer coatings would not eliminate water transport to the Mg anode surface.

#### Electrochemical testing of biodegradable batteries

Figure 5 demonstrates the effect of polymer coatings on the discharge profile and capacity of the Mg/Fe batteries. Uncoated batteries delivered the shortest service life and power, at 2.9 h and 15.5  $\mu$ W, respectively. It was speculated that the hydrogen evolution, as well as the continuous breakdown and formation of the native passive film on the Mg surface, induced stress to the Mg film. The stressing may have been the cause of Mg delaminating from the substrate and consequently causing loss of electrical connection to the current collector. Hence, the polymer coating may provide a secondary purpose of mechanically stabilizing the Mg anode on the substrate.

Batteries coated with 5 and 10 µm of PCL showed higher discharge potentials than uncoated batteries. As expected, electrodes with thicker PCL coatings exhibited increased resistance to charge transfer and provided lower discharge potentials. With increasing polymer thickness, it becomes more difficult for OH<sup>-</sup> ions to travel to the Mg surface. This effect also governed the lifetime of the battery because with thicker polymer films, reaction products accumulated at the PCL-Mg interface with prolonged discharge and corresponded to a decline in discharge potential. This can be observed from batteries coated with 20-µm-thick PCL. Further, hydrogen formation at the Mg anode caused a buildup of internal pressure with thicker PCL membranes. This weakened the adhesion of the PCL film to the substrate and, in some instances, resulted in film delamination.

PGS-coated batteries delivered longer discharge lifetimes than the uncoated batteries. As PGS exhibited higher water permeability and PGS-coated Mg demonstrated lower corrosion potential, it was expected that batteries coated with PGS would also demonstrate better performance than those coated with PCL. This was observed with 10-µm-thick PGS, which showed the highest capacity and coulombic efficiency of 0.7 mA/h and 13.5%, respectively. This discharge lifetime was similar to that of PCL-coated batteries at 5 and 10 um thickness. PGS also provided greater mechanical stability, as thicker PGS films did not delaminate during discharge, as with thicker PCL films. The lower average potential and less stable discharge profile obtained with PGS-coated batteries, especially with increasing polymer thickness, suggested an accumulation of reaction products at the PGS-Mg interface. This was confirmed with X-ray photoelectron spectroscopy (XPS) of PGS-coated batteries after discharge, which showed Mg(OH)<sub>2</sub> in regions where Mg was consumed (data not shown). As such, PGS-coated batteries provided slightly lower power at 25 µA discharge, and the highest power and energy were obtained from PCL-coated batteries. PCL-coated batteries showed a maximum of 26.2  $\mu$ W of power and 2.6 J of energy. As these results fall within the range in power requirements for commercial IMDs, the presented battery chemistries show a promising direction towards providing viable energy sources for powering transient implantable electronics. The range in average discharge potential obtained with batteries coated



Figure 5: Galvanostatic discharge profiles at a current of 25  $\mu$ A. The cutoff potential was 400 mV.

		PCL			PGS		
Passivation	Uncoated	5um	10um	20um	10um	15um	35um
Discharge time (h)	2.9	28.9	26.7	13.6	29.1	14.1	13.6
Capacity (µAh)	73	722	667	341	729	353	341
Power (µW)	15.5	25.3	26.2	22.9	24.8	23.5	25
Energy (J)	0.2	2.6	2.5	1.1	2.6	1.2	1.2
Coulombic efficiency (%)	1.0	13.0	12.0	6.3	13.5	6.6	6.3

*Table 1: Summary of battery performance at a discharge current of 25 \muA.* 

with PGS and PCL, which exceeded the average discharge potential of the uncoated battery, suggested that there exists an optimum coating and thickness for maximizing the power and performance of Mg/Fe batteries. The coating should hinder parasitic corrosion at the Mg anode without appreciably increasing resistance to mass transfer. Further, the coating should be mechanically robust to accommodate for hydrogen evolution at the polymer-Mg interface. Future work may further optimize the use of biodegradable polymer coatings or consider alternative means of enhancing corrosion resistance of the Mg anode. Biodegradable material sets should also be considered for the substrate and packaging. Further design constraints should be governed by the design requirements for a targeted transient disease state.

## CONCLUSIONS

This study comprised the design, fabrication and characterization of a series of MEMS-enabled biodegradable batteries. The underlying principle of the battery operation is the cathodic protection of an evaporated Fe electrode through the oxidation of an electroplated Mg anode in an MgCl<sub>2</sub> electrolyte solution. Two different biodegradable polymer coatings, PGS and PCL, were utilized as passivation layers on the Mg anode to minimize the parasitic degradation of the Mg and, thus, to increase the coulombic efficiency of the system. It was demonstrated that the thickness, as well as the choice of the polymer coating, have a remarkable effect on the battery performance. Thinner coatings yielded higher energy densities while no significant change is observed in power densities. Power and energy values of more than 25 uW and 2.6 J. respectively, were obtained, which fall within range of the reported performance requirements for the commercial IMDs.

## REFERENCES

- Hwang, S.W. *et al.*, "A physically transient form of silicon electronics", *Sci.*, vol. 337, pp. 1640-44, 2012.
- [2] Wei, X. and J. Liu, "Power sources and electrical recharging strategies for implantable medical devices", *Front. Energy Power Eng. China*, vol. 2, pp. 1-13, 2008.
- [3] Luo, M. et al., "A microfabricated wireless RF pressure sensor made completely of biodegradable materials", *Dig. Solid-State Sensors, Actuators, and Microsystems Workshop*, Hilton Head, 2012.
- [4] Morajev, M. and D. Mantovanni, "Biodegradable metals for cardiovascular stent applications: Interests and new opportunities", *Int. J. Mol. Sci.*, vol. 12, pp. 4250-4270, 2011.
- [5] Tsang, M. *et al.*, "Methods for the microfabrication of magnesium", *MEMS 2013*, Taipei, Taiwan, 2013.
- [6] Sundback, C.A. *et al.*, "Biocompatibility analysis of poly(glycerol sebacate) as a nerve guide material", *Biomat.*, vol. 26, pp. 5454-64, 2005.
- [7] Feyerabend, F. *et al.*, "Ion release from magnesium materials in physiological solutions under different oxygen tensions", *J. Mater Sci: Mater Med*, v. 23, pp. 9-24, 2012.
- [8] Ratnakumar, B.V., "Passive films on magnesium anodes in primary batteries", J. App. Electrochem., vol. 18, pp. 268-79, 1988.
- [9] Gill, P. et al., "Corrosion and biocompatibility assessment of Mg alloys", J. Biomat. And Nanobiotech., v. 3, pp. 10-13, 2012.
- [10] Walter, R. *et al.*, "Influence of surface roughness on the corrosion behavior of magnesium alloy", *Mat. And Des.*, v. 32, pp. 2350-54, 2011.

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