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Modulated Degradation of Transient Electronic Devices through Multilayer Silk Fibroin Pockets

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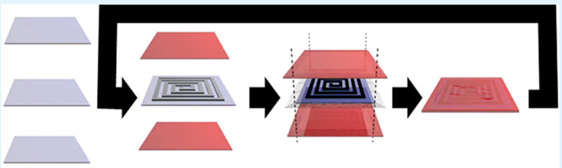
Supporting Information



ABSTRACT: The recent introduction of transient, bioresorbable electronics into the field of electronic device design offers promise for the areas of medical implants and environmental monitors, where programmed loss of function and environmental resorption are advantageous characteristics. Materials challenges remain, however, in protecting the labile device components from degradation at faster than desirable rates. Here we introduce an indirect passivation strategy for transient electronic devices that consists of encapsulation in multiple air pockets fabricated from silk fibroin. This approach is investigated through the properties of silk as a diffusional barrier to water penetration, coupled with the degradation of magnesium-based devices in humid air. Finally, silk pockets are demonstrated to be useful for controlled modulation of device lifetime. This approach may provide additional future opportunities for silk utility due to the low immunogenicity of the material and its ability to stabilize labile biotherapeutic dopants.

KEYWORDS: *silk, fibroin, transient electronics, resorbable, degradation*

The field of bioelectronics has recently benefited from the introduction of "transient" electronics. Transient electronics describe fully resorbable electronic devices that are designed to biodegrade into their environment at predefined time scales, which makes them advantageous for applications where programmed loss of function is desirable.[1,2] In addition to the environmental advantages of biodegradable electronics, bioresorbable devices prepared by this principle show promise for implantable diagnostics and therapeutics, eliminating the need for device retrieval. This attribute suggests a widespread future impact of transient devices in biomedicine.[3] Recent applications of transient devices have included hydration sensors,[4] batteries,[5] RF scavengers,[6] and implantable heaters for infection mitigation.[7]

Despite these advantages, the nature of these devices requires particular attention to their fabrication. The resorbable characteristics are often provided by silicon nanomembranes and magnesium conductors, which are highly water sensitive and degrade in a manner of minutes in wet environments.[8,9] This water sensitivity leads to characteristic device operation that consists of a short period of stable operation followed by rapid degradation at the "transience time" of the device. In this way, transience time is defined by both the device material consituents and the strategy used to protect the device from degrading too quickly.[1]

Common methods of device protection, however, are not without their drawbacks. Direct passivation with a magnesium oxide overlayer has been shown to extend device lifetime to up to 5 days. This extension comes at the expense of mechanical flexibility and with a limited window of control over the rate of degradation.[1,10] Other materials suggested for protection of transient devices, such as chloroform-processed PLA and PVA/gelatin composites, promise tight programmed control of degradation, but the lack of fabrication techniques that integrate these materials with water-soluble electronic components makes their development a challenge.[11,12] Development of additional conducting, semiconducting, and insulating materials is also underway in the hope of extending the transience time of unprotected devices, but the materials in question are unlikely to provide long-term operation by themselves, and they raise concerns about the toxicity and/or

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full bioresobability of the devices.[9] A fully bioresobable nonimmunogenic strategy with the possibility of long-term device survival has not yet been realized.

An excellent candidate for modulation of the transience time of resorbable devices while addressing these concerns can be found in silk fibroin protein. In addition to its use as a transient substrate,[13,14] silk has shown remarkable promise for a number of technical biosensing and biotherapeutic applications in areas such as optics,[15,16] drug delivery,[17,18] and implants.[14,19] This promise stems from the synergistic combination of high mechanical strength, bioresorbability, and minimal immunogenicity found in silk, which matches well with the characteristics of an ideal transient protection material.[20−23] Furthermore, the innate ability of silk to stabilize labile biological entities under unfavorable conditions provides further utility through the potential for hybrid devices.[18] The use of silk fibroin as a passivation material for transient electronic structures could extend their lifetime by acting as a bioresorbable nonimmunogenic diffusional barrier, as well as improving the *in vivo* behavior of the device due to the outer silk layer.[1] This would expand the role of silk-based transient devices for implantable diagnostics and therapeutics.

Protection with silk presents a challenge, however, because of the transient nature of the electronic components. Direct application of a silk passivation layer introduces mechanical stresses to the device materials during drying on a flexible substrate and exposes them directly to water. While this is acceptable for inert, insoluble materials such as gold, it proves problematic for reactive materials such as magnesium and silicon nanomembranes. In this case, the combination of mechanical disruption of the magnesium and rapid degradation causes device failure, making direct passivation with silk (and similar materials) an ineffective strategy (Figure S1).[24]

In this work, we examine an indirect protection strategy for transient devices with silk fibroin, demonstrating modulation of device degradation. A scheme for this strategy is shown in Figure 1a. Transient electronics fabricated by existing techniques on a silk substrate are enclosed within silk films treated to have tunable crystalline and diffusion properties.[25] Sealing the outside of these films through existing thermal processing techniques creates a small air pocket (Figure S2),[16] which provides protection for the water sensitive components of the device. Iteration of this process can provide additional degrees of protection through multiple layer encapsulation as needed. When the construct is exposed to a wet environment, swelling of the silk protective layer collapses the air pocket, causing the onset of device degradation.[26] The collapse process generates two combinations of interfaces as shown in Figure 1b: (1) a silk/air/device interface and (2) a silk/device interface. Control over the material properties of the protective films and the number of layers will ultimately allow tuning of the device transience time.

Degradation "by collapse" offers the advantages of preventing degradation of the delicate transient components during encapsulation, as well as decoupling the fabrication of the device and of the protective pocket for device enclosure. Furthermore, the two independent processes involved allow for added utility through the inclusion of additional components (such as doped or nanostructured films) within the encapsulating layers, and combination of this approach with other existing passivation strategies. Overall, this approach should provide a controllable means of modulating transience time using a fully bioresorbable material with limited immunogenicity.

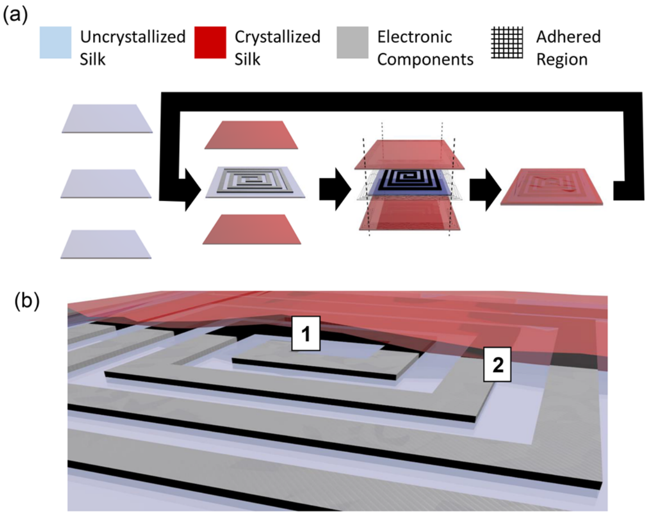

Figure 1. Silk fibroin pocket concept and fabrication strategy. (a) Pocket fabrication strategy. Three uncrystallized silk films are utilized in pocket fabrication. Crystallization of the outer layers renders them water insoluble, while the inner device substrate layer can remain uncrystallized and water-soluble, depending on device fabrication requirements and desired degradation characteristics. Sealing the outer edges around the device encapsulates it in a protective pocket of silk fibroin. Multilayer fabrication is carried out by repeating the process with an inner pocket as the device layer. (b) Pocket concept. Additional control parameters are possible with the addition of a silk/air/device interface [1] to the silk/device interface of traditional passivation [2].

The effect of the silk pocket approach on transience time was first assessed on the benchtop through the study of water transport through the layers of the pocket. A series of systematic experiments were carried out where multilayer silk membranes were used as a barrier to water diffusion from a contained reservoir (Figure 2a). Sealing the sides and top of the reservoir in the experimental setup ensured that water transport (and thus water loss from the reservoir) could only occur from the upper reservoir by passing through the membranes.

Silk membranes to be tested were fabricated through thermal processing to have geometry analogous to the pocket structures being investigated. Laminating only the edges of stacks of 1 to 5 silk films by existing procedures ensured strong interlayer adhesion at the periphery, and poor adhesion in the center.[16] The overall thickness of the silk for each construct was held constant by scaling individual film thickness in inverse proportion to the number of films used to generate the membrane (see Table S1, Figure S2). These structures were analyzed via SEM and optical microscopy (Figure 2b). After adherence to the sample holders and sealing, this configuration allowed for monitoring of water diffusion through a controllable number of silk/air interfaces.

The membranes were then exposed to a wet environment by filling the reservoirs with water. Monitoring of the reservoir volume as the water passed through the silk membranes and into the environment exhibited a linear behavior over a one-week period consistent with steady-state diffusion (Figure S3). Linear fits of these water loss curves were then performed to determine the leak rate (Figure 2c). Notable in these results are the low leak rate magnitudes, which were found to be on the order of microliters per day. Additionally, no liquid water was

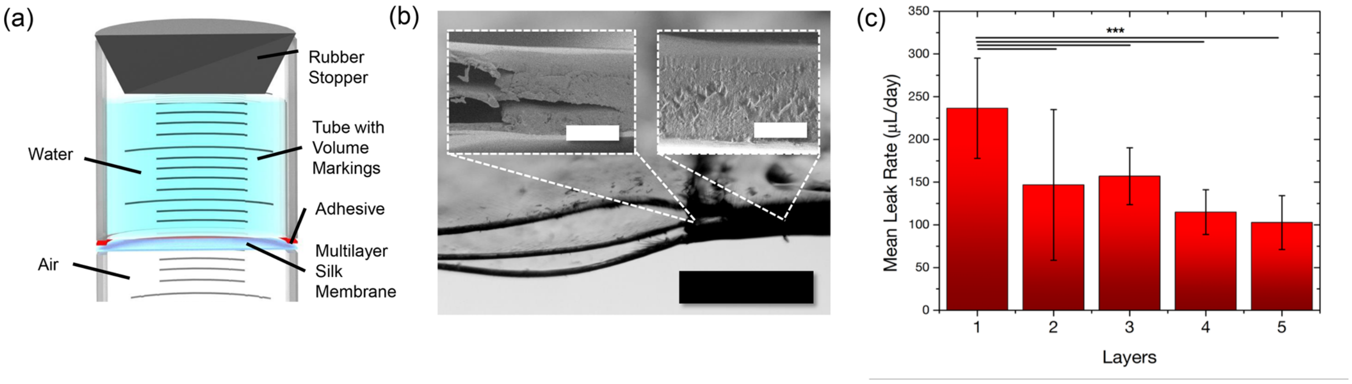

Figure 2. Silk/air interface characteristics, and device behavior experiments with multilayer silk membranes. (a) Schematic of multilayer fabrication with a controlled interface. Crystallized silk is red, and uncrystallized silk is blue. (b) Multilayer membrane cross-section optical and SEM image, as fabricated through utilization of the lamination method, based on Figure S2. Black scale bar represents 1 mm; white scale bars represent 100 μm. (c) Water penetration through multilayer silk membranes as measured by evaporation from sealed tubes over 2 weeks. Starred groups were significant to $p < 0.05$ by Tukey's test. Means were determined significant by one-way ANOVA.

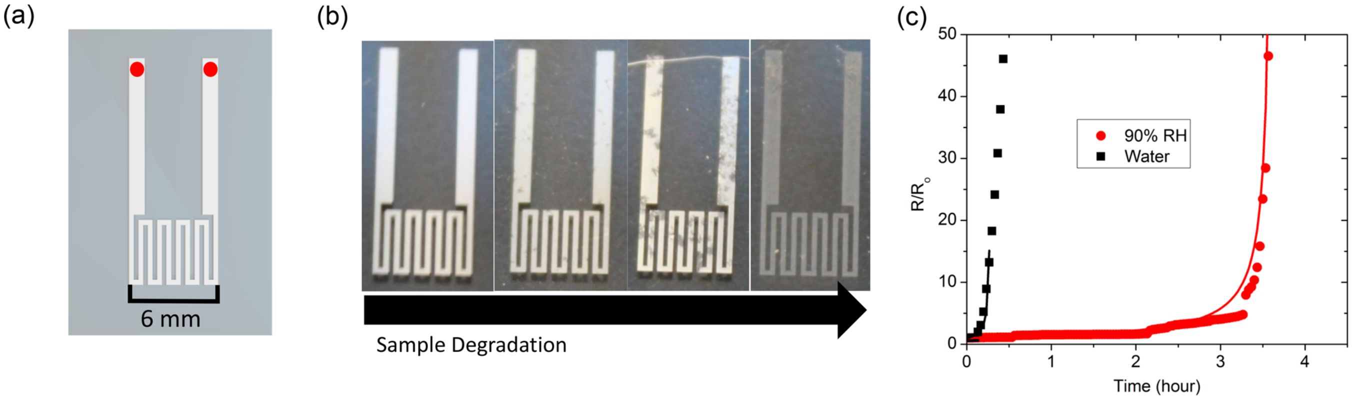

Figure 3. Magnesium degradation behavior at silk/air/device interface. (a) Sample design for resistor degradation test. (b) Images of magnesium resistor traces degraded in a high relative humidity environment show uneven degradation by islands. (c) Resistance of degraded magnesium traces over time with degradation high relative humidity conditions. Experimental results are fit with the existing analytical model for reactive diffusion based magnesium degradation.

collected after passing through the silk membranes at any time. This suggests that the water losses measured were due to evaporation from the exposed underside of the silk membranes. The evaporative-only behavior can be explained by the high surface tension of water (72 mN/m) and the well-studied nanoscale pore size within a hydrated silk film (surface roughness ∼5 nm).[27] The capillary force was enough to hold the liquid water within the swollen film.

Based on this evaporative mechanism, in a multilayer pocket construct, the environment between the layers contains high humidity air with little to no liquid water, and water movement through contiguous, successive layers is affected by the mechanical collapse of the hydrated films. When this collapse occurs, the direct contact between adjacent layers accelerates the diffusion of water in comparison to the humid air environment. Device lifetime will therefore be determined by the number of layers.

This explanation correlates well with the experimental results. As Figure 2c shows, a decrease in the leak rate of the membranes was seen with the addition of each subsequent layer. Strict linear behavior was not observed, but this can be attributed to differences in the mechanical collapse behavior of films of differing thickness, leading to different spatial variation in the two types of interfaces (Figure 1b). Future study of the collapse mechanics of hydrated silk membranes could help to optimize the control of degradation through the additional use of film thickness and patterning as protection parameters.

The humid environment within the pocket also directly affects the degradation rate of the encapsulated transient device through the silk/air/device interface. This effect was evaluated by monitoring the degradation of magnesium layers under humid conditions, with an approach similar to previous work.[1,9,28] Magnesium resistor traces were fabricated on glass slides with dimensions shown in Figure 3a, and placed either in a high relative humidity environment or in direct contact with water (Figure S4). Images of the degradation behavior of these magnesium resistors are shown in Figure 3b. Degradation under humid conditions occurs began preferentially in specific locations and spreads outward. These locations likely correspond to nucleation sites for physical adsorption of water onto the magnesium layer.[29] Degradation kinetics followed nearly identical behavior to previous analytical modeling results with a much slower degradation rate, which was confirmed by fitting the results to the existing model (Figure 3c).[28] The results of these experiments demonstrate that the use of a contact-free passivation approach can control device transience by slowing water penetration and replacing direct water contact with high relative humidity environments.

The benchtop experiments were then leveraged to test the silk pocket approach in a proof-of-principle experiment with

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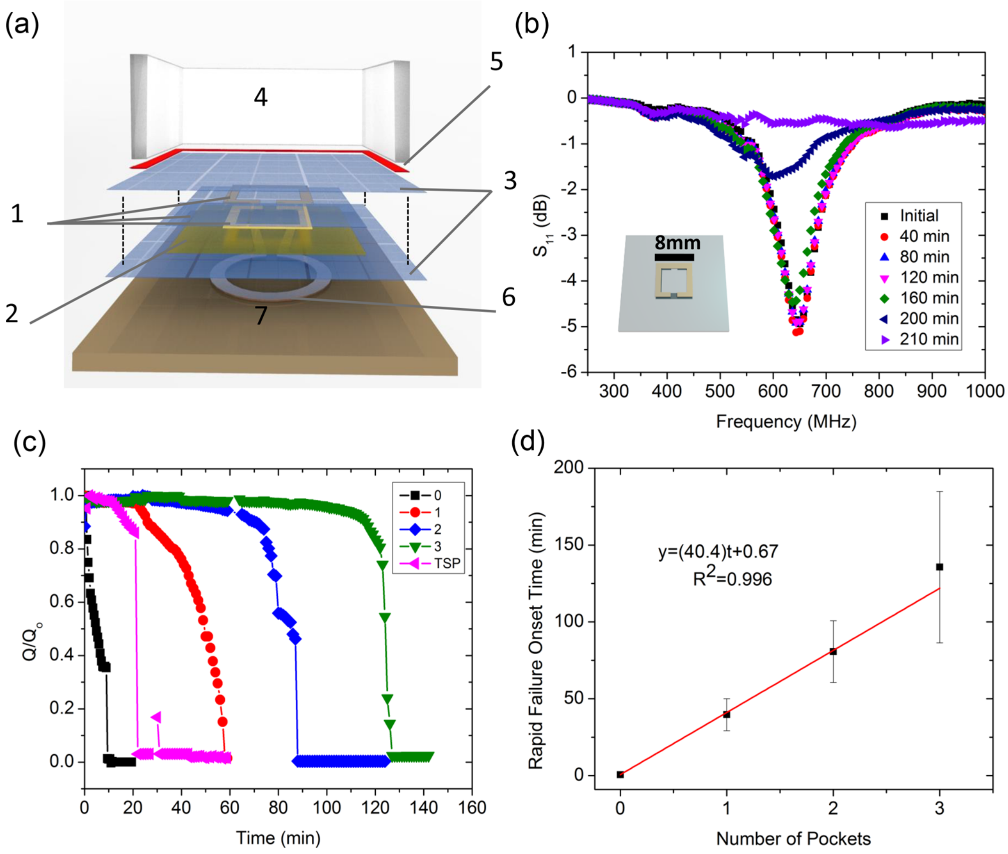

Figure 4. Proof of concept device degradation. (a) Schematic of sample fabrication for the in vitro degradation test. [1] Device consists of an 8 mm passive metamaterial antenna with magnesium upper layer, crystallized silk substrate, and gold lower layer. [2] Polyimide protection of the gold layer prevents device failure due to mechanical disruption of gold. [3] Device encapsulated in silk pockets (0, 1, 2, or 3). [4] Acrylic wells placed above the pocket and edges are attached with [5] adhesive. [6] Device placed on top of complementary copper transceiver antenna fabricated on [7] PCB base, and attached to the network analyzer for constant monitoring of the encapsulated device. During degradation, 1 mL of DI water is added to the well. (b) Characteristic device degradation behavior over time, showing loss of resonant response, and slight downfield shift of resonance with swelling of silk substrate. (c) Calculated change in quality factor over time for degraded encapsulated device. Each curve is a representative sample from 0, 1, 2,and 3 pocket groups. Traces are normalized by dividing by initial value. TSP conditions represent 1 layer pocket of equivalent silk thickness to the 3 layer condition. (d) Increase in time to rapid degradation with additional pocket protection. Linear fit to $R^2 = 0.996$. Means are significant by one way ANOVA and Tukey's test $p < 0.05$.

functioning devices. Simple passive split-ring resonator antennas fabricated in magnesium on silk substrates were measured *in situ*, during the degradation process, using the sample design shown in Figure 4a, and Figure S5. Antenna devices (1, 2) were encapsulated in silk pockets (3) and affixed to an acrylic well (4, 5). Pockets were fabricated in nested geometries with 1, 2, and 3 layers, each of equivalent thickness. During the experiment, deionized water was added to the wells and the resonant response of the encapsulated antenna was monitored at 1 min intervals using a transceiver antenna (6, 7) until the signal was lost (Figure 4b). The initial resonance at 650 MHz decreased in amplitude but not in frequency over time, with the exception of a small shift to lower frequencies that can be explained by the swelling of the silk substrate and the increased dielectric contribution of water.

Antenna quality factors were calculated in an attempt to quantify the degradation behaviors. Degradation exhibited characteristic transient behavior in all cases, with an initial phase of stable operation followed by rapid degradation at the device transience time (Figure 4c).[1] The initial phase is likely due to the slow penetration of water as a consequence of the (multiple) air interfaces, followed by rapid device degradation once wetting and collapse of the pocket into silk/device interfaces takes place.

A single layer pocket with equivalent silk thickness to the total three layer system was also tested as a control (Figure 4c, TSP). This test allowed the effects of silk thickness and number of silk/air interfaces to be compared separately with respect to their influence on device transience. The figure shows that the TSP device degraded in a time frame comparable to that of the 1-layer pocket, despite the 3-fold increase in silk barrier thickness. As mentioned previously, the slightly faster degradation in this time can be attributed to the differing collapse mechanics of the pocket as the thickness of the wetted silk film changes. This result further supports the model of water penetration into the system, as well as the importance of multiple air interfaces in slowing device degradation as compared to individual layer thickness. This conclusion is further supported by our prior work on water penetration and rehydration kinetics with respect to the release kinetics of entrained biologicals in silk structures related to silk density.[30]

To further analyze the behavior, the transience time was estimated for each sample by identifying the point at which degradation exceeded 3% per minute. Figure 4d presents a comparison of transience times by number of pockets, showing a remarkably linear behavior. Each subsequent pocket represents the addition of an identical silk/air interface to the protection scheme. A linear increase in survival time with additional interfaces therefore makes sense, since the mechanics of silk film collapse are similar in all cases.

The measured time scales of device degradation are rapid, but this is likely due to the device composition, which consists of a single 300 nm thick layer of magnesium metal. The transience time of this device would be nearly immediate without protection, and each silk pocket has lengthened the device survival by a factor of approximately 40×. In practice, the combination of the demonstrated silk pocket method with other direct passivation layers could extend device lifetime due to the ability of the silk/air interface to slow water penetration. This makes silk pockets a versatile option for use in modulating the transience time of degradable electronic devices.

In conclusion, we introduced a silk-based passivation strategy to modulate the degradation of transient electronic devices, consisting of indirect encapsulation of the device in a silk pocket system. Investigation of the water transport properties of this system allows this method to be adopted for device protection by minimizing direct water contact with the transient device in exchange for humid air. The exchange leads to controllable device degradation times through multiple silk/air interfaces, as demonstrated using multilayer silk pockets. This encapsulation strategy decouples the fabrication and passivation of transient devices and should improve their *in vivo* response through an external silk layer.[23] With further study, silk pockets may provide opportunities for additional functionality through stabilization of biomolecules within the silk matrix,[18] and may be combined with existing passivation methods and optimized collapse mechanics to further extend the lifetime of this class of devices. Through both the increased control over device degradation rates and the properties of silk as a biomaterial, silk pockets add versatility to the field of transient and implantable electronics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06059.

> Experimental details, supplemental figures, and additional experiments regarding direct passivation of transient devices with silk (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

RF, radio frequency; PVA, poly(vinyl alcohol); SEM, scanning electron microscopy

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