An Analytical Model of Reactive Diffusion for Transient Electronics

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Transient electronics is a class of technology that involves components which physically disappear, in whole or in part, at prescribed rates and at programmed times. Enabled devices include medical monitors that fully resorb when implanted into the human body (“bio-resorbable”) to avoid long-term adverse effects, or environmental monitors that dissolve when exposed to water (“eco-resorbable”) to eliminate the need for collection and recovery. Analytical models for dissolution of the constituent materials represent important design tools for transient electronic systems that are configured to disappear in water or biofluids. Here, solutions for reactive-diffusion are presented in single- and double-layered structures, in which the remaining thicknesses and electrical resistances are obtained analytically. The dissolution time and rate are defined in terms of the reaction constants and diffusivities of the materials, the thicknesses of the layer, and other properties of materials and solution. These models agree well with the experiments for single layers of Mg and SiO₂, and double layers of Mg/MgO. The underlying physical constants extracted from analysis fall within a broad range previously reported in other studies; these constants can be extremely sensitive to the morphologies of the materials, temperature, and the PH value, concentration, and properties of the surrounding liquid.

1. Introduction

Typically, the development of an electronic system involves efforts to optimize the time duration of stable performance of the constituent devices, i.e., their physical and functional lifetimes. The materials and design layouts must be engineered carefully to meet this goal. A different kind of technology, referred to as transient electronics,\[1\] has, as a key characteristic, an opposite feature: it physically disappears at prescribed rates in a benign way when exposed, for example, to water in the environment or the body. Devices built in this manner create application opportunities that lie outside those that can be addressed using established classes of integrated circuits. Examples include medical monitors, interventional components or therapeutic vehicles that fully resorb when implanted into the human body (“bio-resorbable”) to avoid long-term adverse effects. Others involve environmental monitors/sensors that dissolve when exposed to water (“eco-resorbable”) to eliminate the need for collection and recovery.

The approaches reported by Hwang et al.\[1\] create foundations for a silicon based transient technology that can offer excellent performance, in a manner that leverages much of the scientific knowledge and engineering capabilities that have emerged from decades of fundamental and applied work on traditional forms of silicon electronics. When taken together with

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The height of the material is given, which in turn gives the resistance (per unit length) of Mg conductors. The results are compared with experiments, and the validated analytical model not only provides important insights of the transient behavior of the device, but is also useful as design guidelines.

In transient electronic systems, a period of stable operation defined typically by dissolution of the encapsulation layers is followed by functional degradation in a narrow time interval defined by dissolution of electrode itself. First, we introduce a single-layer reactive diffusion model in Section 2 for dissolution of porous materials, such as Mg (as electrodes) or SiO₂ (as dielectrics). A double-layer reactive diffusion model is established in Section 3 for the double-layer structure where the encapsulation layer (MgO) is on top of the porous material (Mg).

### 2. Single-Layer Reactive Diffusion

The process begins when a layer of porous material (e.g., Mg or SiO₂) is submerged in water (or PBS solution). The initial layer thickness \( h_0 \) is much smaller than the layer width/length such that the one-dimensional reactive diffusion model can be applied in the thickness direction \( y \) (Figure 2a), with \( y = 0 \) at the bottom of the layer. The reactive diffusion equation is

\[
D \frac{\partial^2 w}{\partial y^2} - k w = \frac{\partial w}{\partial t}, \quad 0 \leq y \leq h_0
\]

Surface reaction may be enough to account for the dissolution of materials in crystalline structure as in Si [6] or other chemical reactions with large reaction constants, such as oxidation of magnesium, [7] corrosion of iron [8] and burning of wood [9]. However, diffusion becomes important for porous materials such as Mg, MgO deposited by electron beam evaporation, and SiO₂ deposited by plasma enhanced chemical vapor deposition, as shown in Figure 1. Here, the kinetics in alkaline solutions is described analytically using models of reactive diffusion [10] in which the rate limiting step is defined by diffusion of water and hydroxide ions into the porous material and reaction throughout the thickness direction.

This paper applies the reactive diffusion model [10] to the transient electronic systems. An analytical solution of the remaining
where $D$ and $k$ are the diffusivity of water and reaction constant between the porous material and water, respectively. $w$ is the water concentration that depends on position $y$ and time $t$. The above equation degenerates to the standard diffusion equation when the reaction term $kw$ is neglected. For 5 mol% Fe-activated Mg, the reaction constant $k$ ranges from 0.2 × 10^{-3} to 3 × 10^{-3} s^{-1}, [11] depending on the chloride ion concentration from 0 to 5 M in water. Besides ion concentration, $k$ also depends on many other factors such as the morphologies of the materials, temperature, and the pH value, concentration, and properties of the surrounding liquid.

Water concentration is constant $w_0$ at the interface between water and porous material whereas the water flux at the bottom surface of the porous material layer is zero, i.e.,

$$w|_{y=h_0} = w_0$$

$$\left. \frac{\partial w}{\partial y} \right|_{y=0} = 0$$

(2a,b)

The initial condition is zero water concentration, i.e.,

$$w|_{t=0} = 0 \quad (0 \leq y < h_0)$$

(3)

For the new variable $\theta = w - w_0$, Equation (1) – Equation (3) become

$$D \frac{\partial^2 \theta}{\partial y^2} - k \theta - \frac{\partial}{\partial t} \lambda w_0, \quad 0 \leq y \leq h_0$$

(4)

$$\theta|_{y=h_0} = 0$$

$$\left. \frac{\partial \theta}{\partial y} \right|_{y=0} = 0$$

(5a,b)

$$\theta|_{t=0} = -w_0 \quad (0 \leq y < h_0)$$

(6)

The homogeneous solution $\theta_h$ of Equation (4), $D \frac{\partial^2 \theta_h}{\partial y^2} - k \theta_h - \frac{\partial \theta_h}{\partial t} = 0$, and homogeneous boundary conditions $\theta|_{y=h_0} = 0$ and $\partial \theta_h/\partial y|_{y=0} = 0$ from Equation (5) can be solved by the method of separation of variables

$$\theta_h = Y(y) T(t)$$

(7)

This gives

$$D \frac{Y''}{Y} - k = \frac{T'}{T} = -\lambda$$

(8)

where $\lambda$ is the eigenvalue to be determined. The solution of Equation (8) is

$$Y = A \sin \left( \sqrt{\frac{\lambda - k}{D}} y \right) + B \cos \left( \sqrt{\frac{\lambda - k}{D}} y \right)$$

$$T = e^{-\lambda t}$$

(9a,b)

where $A$ and $B$ are constants to be determined. The homogeneous boundary conditions become $Y|_{y=h_0} = 0$ and $Y'_y|_{y=0} = 0$, which give $A = 0$ and

$$\cos \left( \sqrt{\frac{\lambda - k}{D}} h_0 \right) = 0$$

(10)

Its solution gives the eigenvalues

$$\lambda_n = \left( \frac{2n - 1}{2h_0} \pi \right)^2 D + k \quad (n = 1, 2, 3, \ldots)$$

(11)

The homogeneous solution is

$$\theta_h = \sum_{n=1}^{\infty} \left[ b_n e^{-\left( \frac{n-1}{2h_0} \right)^2 D t + \frac{1}{2} \left( \frac{n-1}{2h_0} \right)^2 \frac{\pi^2}{D} } \cos \left( \frac{2n - 1}{2h_0} \pi y \right) \right]$$

(12)

where the constants $b_n$ are to be determined.

The general solution of Equation (4) is the sum of homogeneous solution in Equation (12) and a particular solution,

$$\theta = \sum_{n=1}^{\infty} \left[ b_n e^{-\left( \frac{n-1}{2h_0} \right)^2 D t + \frac{1}{2} \left( \frac{n-1}{2h_0} \right)^2 \frac{\pi^2}{D} } \cos \left( \frac{2n - 1}{2h_0} \pi y \right) \right] + w_0 \left[ \frac{\cosh \left( \sqrt{\frac{k h_0}{D}} \frac{y}{h_0} \right)}{\cosh \left( \sqrt{\frac{k h_0}{D}} \right)} - 1 \right]$$

(13)

where the last term is a particular solution that satisfies Equation (4) and Equation (5). Substitution of Equation (13) into the initial condition in Equation (6) gives

$$B_n = \frac{4 \left( -1 \right)^n \left( 2n - 1 \right) \pi \lambda w_0}{4k h_0^2 + \left( 2n - 1 \right)^2 \pi^2 D}$$

(14)

These give the solution of Equation (1) as

$$w(y, t) = w_0 \left[ \frac{\cosh \left( \sqrt{\frac{k h_0^2}{D}} \frac{y}{h_0} \right)}{\cosh \sqrt{\frac{k h_0^2}{D}}} \right]$$

$$+ 2 \sum_{n=1}^{\infty} \left( -1 \right)^n \left( n - \frac{1}{2} \right) \pi \left( \frac{1}{D} \right)^{\frac{1}{2}} \left( \frac{n-1}{2h_0} \right)^2 \left( \frac{1}{D} \right)^{\frac{3}{2}} \cos \left( \frac{n-1}{2h_0} \left( \frac{1}{2} \right) \pi y \right) \right]$$

(15)

It clearly shows the scaling law that the normalized water concentration, $w/w_0$, depends on the normalized position $y/h_0$, normalized time $D t / h_0^2$ that scales with the diffusivity $D$, and a single non-dimensional parameter $k h_0^2 / D$ that scales with the ratio of reaction constant $k$ to diffusivity $D$, i.e.,

$$\frac{w}{w_0} = \tilde{w} \left( \frac{y}{h_0}, \frac{D t}{h_0^2}, \frac{k h_0^2}{D} \right)$$

(16)

where $\tilde{w}$ is a non-dimensional function obtained from Equation (15). For $k h_0^2 / D = 0.18$, which corresponds to $k = 1.2 \times 10^{-3} \text{s}^{-1}$ that falls within the range of reaction constants reported by Taub et al., [12] $D = 6.0 \times 10^{-12} \text{cm}^2 \text{s}^{-1}$, and $h_0 = 300 \text{nm}$ of Mg in the experiment, Figure 3 shows the distribution of water concentration for the normalized time $D t / h_0^2 = 0.1, 0.2, 0.4, 0.8, 2$ and $\infty$, where $D t / h_0^2 = \infty$ corresponds to the steady-state limit.
of water that reacts at a given location (per unit volume), the mass of dissolved porous material (per unit volume) is \( kw M / (q M_{H_2O}) \), where \( M \) and \( M_{H_2O} \) are the molar masses of porous material and water, respectively. The net mass of porous material dissolved is obtained by integrating Equation (15) over both the thickness direction \( y \) and time \( t \), where in turn gives a scaling law of the thickness \( h \) of the porous material layer normalized by its initial thickness \( h_0 \) before complete physical disappearance as

\[
\frac{h}{h_0} = 1 - \frac{w_0 M}{q \rho M_{H_2O}} \frac{k h_0^2}{D} + \frac{1}{\sqrt{D t}} \frac{\int h_0^2}{\sqrt{D t}}
\]

which is effectively attained at finite time \( Dt / h_0^2 \). Figure 4 shows the water concentration versus time at the middle \( y = h_0 / 2 \) and bottom \( y = 0 \) of the layer. It confirms that the steady-state limit is reached at \( Dt / h_0^2 = 2 \).

Let \( q \) denote the number of water molecules that react with each atom of the porous material. Since \( kw \) gives the mass density of porous material, its rate is the critical time for the thickness to reach zero. For Mg (molar mass \( M = 24 \text{ g mol}^{-1} \), mass density \( \rho = 1.738 \text{ g cm}^{-3} \)) with the initial thickness \( h_0 = 300 \text{ nm} \) to react with water (molar mass \( M_{H_2O} = 18 \text{ g mol}^{-1} \), water concentration \( w_0 = 1 \text{ g cm}^{-3} \), and \( q = 2 \) water molecules reacting with 1 Mg atom), this critical time \( t_c \) is 38 min, which agrees reasonably well with experiments, to be discussed in Figure 5. Equation (20) shows that the thickness decreases linearly with time. Therefore, the rate of dissolution is

\[
u_{\text{dissolution}} = -\frac{dh}{dt} \approx \frac{h_0}{t_c} = \frac{k h_0^2}{\sqrt{D t}} \frac{w_0 M}{q \rho M_{H_2O}} \tanh \left( \frac{k h_0^2}{\sqrt{D t}} \right)
\]

As shown in Table 1, the rate of dissolution is 0.044, 0.13, and 0.20 nm s\(^{-1}\) (or equivalently 160, 470, and 710 nm h\(^{-1}\)) for 100, 300, and 500-nm-thick Mg layers, respectively. They are on the same order as the rate of dissolution reported in...
experiments, such as 0.069 nm s\(^{-1}\) in the citric acid-Na:\(_2\)HPO\(_4\) buffer system with pH 7.4\([\text{12}]\) and 0.096 nm s\(^{-1}\) in conventional chloride solution.\([\text{13}]\) However, the rate of dissolution depends strongly on the surrounding liquid, such as 0.48 nm s\(^{-1}\) in the 0.125 M NaCl,\([\text{14}]\) 1.3–2.9 nm s\(^{-1}\) in the normal simulated body fluid (SBF),\([\text{15}]\) and as high as 940 nm s\(^{-1}\) in 0.3 M MgCl\(_2\).\([\text{16}]\) Equation (21) and Equation (22) show the important scaling laws for all materials properties that come into play.

The electric resistance (per unit length) is inversely proportional to the thickness and is given by

\[
R = \frac{R_0}{h} = \frac{R_0}{1 - \frac{t}{t_c}}
\]

(23)

where \(R_0\) is the initial resistance (per unit length). For Mg with the initial thickness \(h_0 = 300\) nm and initial resistance (per unit length) \(R_0 = 1.06\) \(\Omega\) mm\(^{-1}\) to react with water, Figure 5 shows the normalized electric resistance \(R/R_0\) versus the normalized time \(t/t_c\). The analytical result from Equation (23) agrees well with the experiments for the reaction constant \(k = 1.2 \times 10^{-3}\) s\(^{-1}\) and diffusivity \(D = 6.0 \times 10^{-12}\) cm\(^2\) s\(^{-1}\). The critical time \(t_c\) for complete dissolution of Mg is 38 min obtained from Equation (21), which agrees well with 40 min for open circuit in experiments. It should be pointed out that the dissolution of Mg may involve an initial layer of MgO on the surface, which will be quickly replaced by the more stable hydroxide in the presence of water.\([\text{17}]\) This thin Mg(OH)\(_2\) film on Mg is generally regarded as crystalline and is not as protective as non-crystalline films,\([\text{18}]\) thereby suggesting that the single-layer dissolution model is applicable to Mg.

### Table 1. Dissolution rate in water [nm h\(^{-1}\)].

<table>
<thead>
<tr>
<th>Initial thickness [nm]</th>
<th>Mg</th>
<th>Mg/MgO (400 nm)</th>
<th>Mg/MgO (400 nm) + silk</th>
<th>Mg/MgO (800 nm)</th>
<th>Mg/MgO (800 nm) + silk</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>160</td>
<td>52</td>
<td>28</td>
<td>15</td>
<td>1.5</td>
</tr>
<tr>
<td>300</td>
<td>470</td>
<td>85</td>
<td>47</td>
<td>23</td>
<td>2.3</td>
</tr>
<tr>
<td>500</td>
<td>710</td>
<td>96</td>
<td>53</td>
<td>26</td>
<td>2.6</td>
</tr>
</tbody>
</table>

For dissolution of PECVD SiO\(_2\) dielectric (molar mass \(M = 60\) g mol\(^{-1}\), mass density \(\rho = 2.648\) g cm\(^{-3}\)) with the initial thickness \(h_0 = 35, 70,\) and 100 nm in water (molar mass \(M_{\text{H}_2\text{O}} = 18\) g mol\(^{-1}\), water concentration \(w_0 = 1\) g cm\(^{-3}\), and \(q = 2\) water molecules reacting with 1 SiO\(_2\) molecule), the diffusivity and reaction constant between water and PECVD SiO\(_2\) dielectric are obtained from the experiments as \(D = 1.0 \times 10^{-16}\) cm\(^2\) s\(^{-1}\) and \(k = 1.5 \times 10^{-6}\) s\(^{-1}\) at room temperature, and \(D = 2.0 \times 10^{-16}\) cm\(^2\) s\(^{-1}\) and \(k = 3.0 \times 10^{-6}\) s\(^{-1}\) at body temperature. These values of \(D\) fall within the range of diffusivity reported in experiments\([\text{19-26}]\) which depends on the temperature. Here \(k\) for SiO\(_2\) \((-10^{-6}\) s\(^{-1}\)\) is much smaller than that for Mg \((-10^{-3}\) s\(^{-1}\)\) because the water-Mg reaction is much faster (minutes to dissolve Mg versus days to dissolve SiO\(_2\)). The non-dimensional parameters are \(w_0 M/(q \rho M_{\text{H}_2\text{O}}) = 0.63\) and \(kh^2/D = 0.18\), 0.74 and 1.5 for three initial thicknesses and room temperature. Figure 6 shows the normalized thickness \(h/h_0\) of SiO\(_2\) at room temperature versus normalized time \(Dt/h_0^2\) as defined in Equation (16). The analytical results from Equation (18) agree well with experiments for all three initial thicknesses. The critical time to dissolve SiO\(_2\) with initial thickness of 35, 70, and 100 nm is 13, 15, and 18 days, respectively, which agree reasonably well with experiments shown in Figure 6. The corresponding rates of dissolution are 0.11, 0.19, and 0.23 nm h\(^{-1}\) at room temperature, respectively, and they increase to 0.22, 0.39, and 0.47 nm h\(^{-1}\) at the body temperature. These rates for PECVD SiO\(_2\) are consistent with the rates reported in prior experiments\([\text{27,28}]\) but are higher than those for quartz.\([\text{29,30}]\)

### 3. Double-Layer Reactive Diffusion

The timeframe to dissolve a layer of Mg with the initial thickness \(h_0\) is defined by the material itself, as given in Equation (21). Figure 2b shows an encapsulation layer of MgO with initial
thickness $h_{\text{encapsulation}}$ to provide another stage that the device functions stably. For the Mg layer, the reactive diffusion equation (1), zero water flux condition at the bottom surface $y = 0$ in Equation (2b), and zero initial condition at $t = 0$ in Equation (3) still hold. For the MgO encapsulation, the governing equation, boundary condition and initial condition are

$$D_{\text{encapsulation}} \frac{\partial^2 w}{\partial y^2} - k_{\text{encapsulation}} w = \frac{\partial w}{\partial t} (h_0 \leq y \leq h_0 + h_{\text{encapsulation}})$$

$$w|_{y=h_0+h_{\text{encapsulation}}} = 0$$

$$w|_{y=0} = 0 (h_0 \leq y \leq h_0 + h_{\text{encapsulation}})$$

(24a-c)

where $D_{\text{encapsulation}}$ and $k_{\text{encapsulation}}$ are the diffusivity and reaction constant between the encapsulation layer (e.g., MgO) and water, respectively. The constant water concentration condition in Equation (2a) is replaced by the continuity of concentration and flux of water molecules across the MgO/Mg interface, i.e.,

$$w|_{y=h_0-0} = w|_{y=h_0+0}$$

$$D_{\text{encapsulation}} \frac{\partial w}{\partial y} |_{y=h_0-0} = D_{\text{encapsulation}} \frac{\partial w}{\partial y} |_{y=h_0+0}$$

(25a,b)

The water concentration $w$ can be represented by a sum of the homogeneous solution $w_h$ and a particular solution $w_p$, i.e., $w = w_h + w_p$. Here the homogeneous solution $w_h$ satisfies the following homogeneous boundary equations and boundary conditions

$$D' \frac{\partial^2 w_h}{\partial y^2} - k'h'_h \equiv 0$$

$$w_h|_{y=h_0+h_{\text{encapsulation}}} = 0$$

$$\frac{\partial w_h}{\partial y} |_{y=0} = 0$$

(26a-c)

where $D' = D$ and $k' = k$ for $0 \leq y \leq h_0$, and $D' = D_{\text{encapsulation}}$ and $k' = k_{\text{encapsulation}}$ for $h_0 \leq y \leq h_0 + h_{\text{encapsulation}}$. The above equation can be solved by the method of separation variables, which gives the solution

$$w_h = \begin{cases} E e^{-\xi y} \sinh \left( \frac{\sqrt{\lambda - k_h}}{D_{\text{encapsulation}}} y \right), & 0 \leq y \leq h_0 \\ F e^{\xi y} \sin \left( \frac{\sqrt{\lambda - k_h}}{D_{\text{encapsulation}}} (h_0 + h_{\text{encapsulation}} - y) \right), & h_0 \leq y \leq h_0 + h_{\text{encapsulation}} \end{cases}$$

(27a,b)

where $E$ and $F$ are constants to be determined. The continuity conditions in Equation (25) is applied to the homogeneous solution, which gives

$$\begin{bmatrix} \cos \left( \frac{\sqrt{\lambda - k_h}}{D_{\text{encapsulation}}} h_0 \right) \\ -\sin \left( \frac{\sqrt{\lambda - k_h}}{D_{\text{encapsulation}}} h_0 \right) \\ -\sqrt{\lambda - k_{\text{encapsulation}} h_{\text{encapsulation}}} \end{bmatrix} \begin{bmatrix} E \\ F \\ E \end{bmatrix} = 0$$

(28)

The vanishing of its determinant, in order to have a non-trivial solution, leads to the following eigen equation

$$\tan \sqrt{\frac{\lambda - k_{\text{encapsulation}}}{D_{\text{encapsulation}}}} \cos \left( \frac{\sqrt{\lambda - k_{\text{encapsulation}}}}{D_{\text{encapsulation}}} h_{\text{encapsulation}} \right)$$

$$\tan \frac{\sqrt{\lambda - k_{\text{encapsulation}}}}{D_{\text{encapsulation}}} = \sqrt{\frac{\lambda - k_{\text{encapsulation}}}{D_{\text{encapsulation}}}} \frac{k_{\text{encapsulation}}}{D_{\text{encapsulation}}}$$

(29)

from which a series of roots $\lambda_n (n = 1, 2, 3, \ldots)$ can be determined. The homogeneous solution can then be obtained as

$$w_h = w_0 \sum_{n=1}^{\infty} C_n e^{-\lambda_n t} f_n(y)$$

(30)

where the coefficients $C_n$, which replace $E$ and $F$ via Equation (28), are to be determined, and

$$g(y) = \begin{cases} G \cosh \left( \frac{\sqrt{\lambda - k_{\text{encapsulation}}}}{D_{\text{encapsulation}}} (h_0 + h_{\text{encapsulation}} - y) \right), & h_0 \leq y \leq h_0 + h_{\text{encapsulation}} \\ H \sinh \left( \frac{\sqrt{\lambda - k_{\text{encapsulation}}}}{D_{\text{encapsulation}}} h_{\text{encapsulation}} \right), & 0 \leq y \leq h_0 \end{cases}$$

(33a,b)

$$G = \frac{1}{\sqrt{D_{\text{encapsulation}} k_{\text{encapsulation}}}} \sinh \frac{\xi h_0}{D} \sinh \frac{\xi h_{\text{encapsulation}}}{D} + \cosh \frac{\xi h_0}{D} \cosh \frac{\xi h_{\text{encapsulation}}}{D}$$

$$H = \frac{1}{\sqrt{D_{\text{encapsulation}} k_{\text{encapsulation}}}} \tanh \frac{\xi h_0}{D} + \tanh \frac{\xi h_{\text{encapsulation}}}{D}$$

(34a,b)

and $\xi = \sqrt{k_{\text{encapsulation}} h_{\text{encapsulation}}^2 / D_{\text{encapsulation}}}$. The water concentration $w$ is the sum of $w_h$ in Equation (30) and $w_p$ in Equation (32),

$$w = w_0 \sum_{n=1}^{\infty} C_n e^{-\lambda_n t} f_n(y) + g(y)$$

(35)
The initial conditions (3) and (20c) require
\[ \sum_{n=1}^{\infty} C_n f_n(y) + g(y) = 0 \]  

(36)

The orthogonality of eigenfunctions \( f_n(y), f_m(y) \) \( \int_0^h f_n(y) f_m(y) dy = 0 \) \( (\text{if } m \neq n) \) gives analytically the coefficient \( C_n \) as
\[
C_n = -\frac{\int_0^{h_0} f_n(y) g(y) dy}{\int_0^{h_0} f_n(y)^2 dy}
\]

\[
= -\frac{2}{\lambda_n} \sqrt{\left(\lambda_n - k_{\text{encapsulation}}\right)} D_{\text{encapsulation}} \sin \left(\frac{\lambda_n h_0}{D_{\text{encapsulation}}}\right)
\]

\[
+ \frac{h_0 \sin^2 \left(\frac{\lambda_n h_0}{D_{\text{encapsulation}}}\right) + h_{\text{encapsulation}} \cos^2 \left(\frac{\lambda_n h_0}{D_{\text{encapsulation}}}\right)}{2 \frac{\lambda_n}{\lambda_n - k_{\text{encapsulation}}}}
\]

(37)

Its substitution into Equation (35) gives the solution of the double-layer reactive diffusion equation. Besides depending on the normalized position \( y/h_0 \), time \( Dt/h_0^2 \), and the non-dimensional parameters \( k h_0^2/D \) as in the single-layer solution in Section 2, the normalized water concentration \( w/w_0 \) also depends on the normalized reaction constant \( k_{\text{encapsulation}} h_{\text{encapsulation}}/D_{\text{encapsulation}} \) of the encapsulation, and the diffusivity ratio \( D_{\text{encapsulation}}/D \) and initial thickness ratio \( h_{\text{encapsulation}}/h_0 \). Figure 7 shows the distribution of water concentration in both layers (\( w/w_0 \) versus \( y/h_0 \)) for \( Dt/h_0^2 = 1.2, 2.4, 4.8, 12, \infty \), and the non-dimensional parameters \( k h_0^2/D = 0.18 \), \( k_{\text{encapsulation}} h_{\text{encapsulation}}/D_{\text{encapsulation}} = 1.6 \), \( D_{\text{encapsulation}}/D = 0.082 \), and \( h_{\text{encapsulation}}/h_0 = 1.3 \), which correspond to \( k = 1.2 \times 10^{-3} \text{ s}^{-1} \), \( D = 6.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1} \), and \( h_0 = 300 \text{ nm of Mg} \) (the same as those in Section 2), and \( k_{\text{encapsulation}} = 5.0 \times 10^{-4} \text{ s}^{-1} \), \( D_{\text{encapsulation}} = 4.9 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1} \), and \( h_{\text{encapsulation}} = 400 \text{ nm of MgO} \) in the experiment. The above diffusivity \( D_{\text{encapsulation}} \) falls within the range \((3.2 \times 10^{-13} \sim 7.9 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1})\) reported in the experiment for MgO,\(^{[31]}\) but is different from the other experiments because of very different temperatures and environments (e.g., Eastman and Cutler\(^{[32]}\) for an isolated water molecule into (001) MgO, McCarthy et al.\(^{[33]}\) for diffusion of \( \text{O}_2 \) into MgO, Leeuw and Parker\(^{[34]}\) for self-diffusion of MgO). The reaction constant of MgO, \( k_{\text{encapsulation}} = 5.0 \times 10^{-4} \text{ s}^{-1} \), is consistent with that extracted from the prior experiments for a single layer MgO.\(^{[35-38]}\) For 100-nm-thick MgO layer, Equation (22) gives the rate of dissolution 0.010 nm s\(^{-1}\), which falls within the range of 0.01-0.01 nm s\(^{-1}\) reported in the experiments. The distribution of water concentration in Mg is quite uniform whereas that in MgO is non-uniform because the diffusion of water in Mg is much faster than that in MgO (e.g., \( D_{\text{encapsulation}}/D = 0.082 \)). As compared to Figure 3 for a single layer, the water concentration in Mg increases slowly because of the encapsulation layer.

In the same manner as described in Section 2, the thickness \( h \) of the Mg layer normalized by its initial thickness \( h_0 \) before complete physical disappearance is obtained as

\[
\frac{h}{h_0} = 1 - \frac{w_0 M}{q \rho M_{\text{H}_2 \text{O}}} k \left[ Gt \cdot \sinh \frac{\sqrt{\frac{\lambda_n^2}{D_{\text{encapsulation}}}}} {\sqrt{\frac{\lambda_n^2}{D_{\text{encapsulation}}}}} \right]
\]

\[
+ \sum_{n=1}^{\infty} C_n \left( 1 - e^{-\lambda_n^2} \right) \sin \frac{\sqrt{\frac{\lambda_n^2}{D_{\text{encapsulation}}}} h_0}{\sqrt{\frac{\lambda_n^2}{D_{\text{encapsulation}}}}} \left[ 1 - e^{-\lambda_n^2} \right],
\]

where \( q = 2 \), molar mass \( M = 24 \text{ g mol}^{-1} \) and mass density \( \rho = 1.738 \text{ g cm}^{-3} \) for Mg, and \( G \) is given in Equation (34a).

The electric resistance (per unit length) of this double-layer structure is inversely proportional to the thickness of Mg layer because MgO is not a conductor. The electric resistance is given analytically by

\[
R = \frac{R_0 h_0}{h}
\]

(39)

For a 300-nm-thick Mg layer with the 400-nm-thick MgO encapsulation layer, the measured initial resistance (per unit length) is 1.04 \text{ \textOmega mm}^{-1}. Another 300-nm-thick Mg layer, which has different width and length and an 800-nm-thick encapsulation layer, has an initial resistance of 1.15 \text{ \textOmega mm}^{-1}. Figure 8 shows the normalized electric resistance \( R/R_0 \) versus the normalized time \( Dt/h_0^2 \) for the single-layered Mg and Mg with 400- and 800-nm-thick MgO encapsulation layers. The thickness of Mg layer is fixed at 300 nm. The analytical results from Equation (38) and Equation (39) agree well with the experiments. The dissolution time increases substantially with the thickness of encapsulation layer, which provides an effective way to control the dissolution time.

In order to further extend the dissolution time a silk overcoat is used to provide a barrier for water to diffuse into MgO.
and Mg layers. The effective diffusion is controlled by the percentage $\varphi$ of the maximum crystallinity $c_{\text{max}}$ that can be achieved in the silk.\textsuperscript{39,40} which gives the crystallinity of silk $c = \varphi c_{\text{max}}$. The boundary condition of the constant water concentration at water/MgO interface in Equation (24b) is then replaced by $w_h|_{y = h_{\text{encapsulation}}} = (1 - \varphi) w_0$. The corresponding solutions are readily obtained by replacing $w_0$ with $(1 - \varphi) w_0$ in this section. For example, the water concentration in Equation (35) becomes

$$ w = (1 - \varphi) w_0 \left[ \sum_{n=1}^{\infty} C_n e^{-x_n t} f_n (y) + g (y) \right] $$

(40)

where $C_n$, $\lambda_n$, $f_n$ and $g$ are still given by Equation (37), Equation (29), Equation (31) and Equation (33), respectively. The electric resistance in Equation (39) also holds, but $w_0$ in Equation (38) for the thickness is replaced with $(1 - \varphi) w_0$. Figure 8 shows the electric resistance for Mg with MgO encapsulation layers and two different silk overcoats with $\varphi = 45\%$ and $90\%$, respectively. Results for a single layer of Mg (Figure 5) are also shown in Figure 8 for comparison. For Mg with 400-nm-thick MgO encapsulation layer and silk overcoat with $\varphi = 45\%$, the dissolution time is about 1.5 times larger than that without the overcoat. For Mg with 800-nm-thick MgO encapsulation layer and silk overcoat with $\varphi = 90\%$, the dissolution time increases substantially to more than 10 times of that without the overcoat. The dissolution time increases with the crystallinity ($\varphi c_{\text{max}}$) because a higher crystallinity provides a stronger barrier for the water to diffuse into MgO and Mg. The analytical results in Figure 8 all agree well with experiments.

The summation on the right hand side of Equation (38) and Equation (40) is negligible for the parameters in the present study such that the thickness decreases linearly with time, and has a simple and approximate expression

$$ \frac{h}{h_0} \approx 1 - \frac{t}{t_c} $$

(41)

where

$$ t_c = \frac{t_c}{(1 - \varphi)} G \cosh \left( \frac{\sqrt{k/\rho}}{D} \right) = \frac{t_c}{1 - \varphi} \left( \frac{k D}{k_{\text{encapsulation}} D_{\text{encapsulation}}} \tanh \left( \frac{\sqrt{k/\rho}}{D} \sinh \xi + \cosh \xi \right) \right) $$

(42)

is the critical time for the Mg layer to reach zero, and $t_c$ is the critical time without the encapsulation given in Equation (21). Equation (42) gives 3.5 and 13 h for the 400-nm- and 800-nm-thick MgO encapsulation layers without the silk overcoat, respectively. With the overcoat they increase to 6.4 and 130 h, respectively. These dissolution times agree well with the time for open circuit in experiments.

Equation (41) gives the rate of dissolution

$$ v_{\text{dissolution}} = -\frac{dh}{dt} \approx \frac{h_0}{t_c} $$

$$ = \frac{(1 - \varphi) \sqrt{k D}}{k_{\text{encapsulation}} D_{\text{encapsulation}}} \sinh \xi + \coth \sqrt{\frac{k D}{D^2}} \cosh \xi $$

(43)

Table 1 shows the dissolution rate for Mg, Mg/MgO, and Mg/MgO+silk. The initial thickness of Mg layer is 100, 300 and 500 nm. The dissolution rate depends strongly on the materials, ranging from $\approx 1$ nm min$^{-1}$ for Mg to $\approx 1$ nm h$^{-1}$ for Mg/MgO (800 nm)+silk. For each material, the dissolution rate is approximately linear with the initial thickness $h_0$ for sufficiently thin Mg layer, and is given by
The dissolution rate increases with the initial thickness $h_0$. For relatively large $h_0$, it saturates at

$$
u_{\text{dissolution}} = (1 - \phi) \frac{\omega_0 M}{4 q M_{11} \phi} \frac{k h_0}{\cosh \xi} \quad \text{for} \quad kh_0^2 / D < 1. \quad (44)$$

$$
u_{\text{dissolution}} = \left(1 - \phi\right) \frac{\sqrt{D} \frac{m_g M}{4 q M_{11} \phi} \frac{k h_0^2}{D \phi}}{\sqrt{\nu_{\text{recapulation}} \nu_{\text{dissolution}}} \sinh \xi + \cosh \xi} \quad \text{for} \quad kh_0^2 / D \gg 1 \quad (45)$$

4. Concluding remarks and discussion

Analytical models for the transient electronic systems have been established. For single- and double-layered structures (with or without the silk overcoat) in solution, the remaining height and electric resistance of the system are obtained analytically. In particular, the dissolution time and rate of dissolution are given analytically in terms of the reaction constant and diffusivity of each material in the solution, molar masses and mass density of materials and solution, solution concentration, number of solution molecules reacting with each atom, crystallinity of silk overcoat, and thickness of each layer. The analytical models agree well with the experiments for Mg single layer, MgO/MgO double layer (with and without overcoat), and are useful for design of transient electronic components.

The model of reactive diffusion can also be applied at the system level. To demonstrate this capability, in vivo transience of an implantable RF metamaterial antenna is tested. The quality factor or Q factor measured in experiments, which describes how under-damped a resonator is, or equivalently, characterizes a resonator’s bandwidth relative to its center frequency, also agrees well with the analytical models. \[1\]

It should be pointed out that the range of reaction constant reported in the literature is very large because it depends on many factors that can vary vastly in experiments, such as morphologies of the materials, temperature, and the pH value, concentration, and properties (e.g., ion concentration) of the surrounding liquid. The reaction constants and diffusivities reported in this paper for Mg, MgO, and SiO$_2$ are close to, or on the same order as, those reported in the literature under similar conditions. However, any of these constants can be extremely sensitive to the conditions so that those provided in this paper do not have to be universal.

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