Biomedical Implant Corrosion
Passivation Using PAMAM
Dendrimer Films

Team Captain: Ben Jones
Design and Modeling: Elizabeth Ashley
Modeling: Kerry Toole
Prototyping and Secretary: Rachel Stein
Treasurer: Mari Hagemeyer
• Background and Motivation
• Project Design Goals
• Technical Approach
• Modeling Results
• Prototyping
• Experimental Results
• Conclusion
Background

- Ti/TiO₂ is widely used for biomedical implants
- Passivation generally achieved by allowing the Ti to grow a native oxide layer
- Problem: oxide can corrode by pitting
  - Driven by concentration gradients of dissolved Cl⁻ and O₂
  - Pits expose reactive Ti metal below oxide
Background

• Dendrimers are fractal, branched polymers
  – Steric hindrance and electrostatic repulsion cause globular shape and cavities

• Densely packed branches act as a diffusion barrier

• PAMAM – Poly(amidoamine)
Design Proposal

• Design a PAMAM dendrimer monolayer to passivate TiO$_2$ from pitting corrosion
• Model the diffusion of chloride ions in aqueous solution through PAMAM to TiO$_2$ surface using Kinetic Monte Carlo
• Investigate the diffusion of Ti ions from the sample through the dendrimer into a physiological solution
MODELING AND SIMULATIONS

- Kinetic Monte Carlo Theory
- MATLAB Simulations
- Basic Approach
- Limitations
- Results
Initial System

- Dendrimer film
  - Emulated by layered planes
  - Approximated as truncated cube
- Cl- ion solution
  - Random
- Total constraining volume
  - x*y*z 3D matrix
- Boundary constraints
  - No particles at system edge
• Two basic types: orthogonal and diagonal
  – 36 total possible directions defined
  – Single- and double-hops in each basic direction
• Greater physical realism
• Hopping probabilities determined relative to orthogonal using geometric ratios and Hooke’s Law
Choosing a Hopping Direction

- Determine occupancy of 36 possible directions relative to ion
- Assign hopping probability
- Randomly select a hopping direction from available sites

For directions right and right2 and probabilities $p_1$ and $p_2$:

1. \([ \text{right} \atop \text{right2} ] = [0] \quad [p_1 \atop p_2] = \begin{bmatrix} p_{\text{Fluid}} \\ p_{\text{Fluid2}} \end{bmatrix} \)

2. \([ \text{right} \atop \text{right2} ] = [0] \quad [p_1 \atop p_2] = \begin{bmatrix} p_{\text{Fluid}} \\ 0 \end{bmatrix} \)

3. \([ \text{right} \atop \text{right2} ] = [1] \quad [p_1 \atop p_2] = \begin{bmatrix} 0 \\ p_{\text{Fluid2}} \end{bmatrix} \)

4. \([ \text{right} \atop \text{right2} ] = [n] \quad [p_1 \atop p_2] = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \)

5. \([ \text{right} \atop \text{right2} ] = [2] \quad [p_1 \atop p_2] = \begin{bmatrix} 0 \\ p_{\text{Branch}} \end{bmatrix} \)
• Time step: fs
• Iterations: 2000
• Plot: ion distribution per time step
  – Ions in dendrimer film
  – Ions through dendrimer film

xyz = 40 x 40 x 20
Total ion count: 3000
Advantages
• Conceptually simple
• Intuitive mathematical expression
• Scalable level of complexity
• Concise plotting features

Disadvantages
• Computationally expensive
  – Impractical to simulate actual experimental duration
  – Must increase Cl-ion concentration for results
• System “lattice”: not realistic
• Dendrimers: not identical or cubic
Results

Control

- $10^6$ iterations gave 1761 ions through substrate

Dendrimer Film

- Cl- ions enter film, but none diffuse through to opposite side during simulation time
  - Extrapolation: film effectively serves as a diffusion barrier to ion penetration
PROTOTYPING

- Sputtering and Oxidation
- Dendrimer Film Formation
- Corrosion Testing
- Ellipsometry
- SEM/EDS
- ICP-OES
- Data Analysis
Sputtering and Oxidation

- Required: prototype surface smooth enough for characterization
  - Sputtered ~ 1 μm Ti metal onto Si substrate

- Two oxidation techniques:
  - Thermal: heat samples in an oven under O₂ gas at 700 °C for 1 hour
  - Plasma-enhanced: bombard samples with O₂ plasma at 400 °C for 2 minutes
Dendrimer Film Formation and Corrosion Testing

Fabrication procedure

• 0.39 μm G5 PAMAM dendrimer in methanol

• Submerge titanium oxide surfaces in solution for 2 hours with agitation

• Allow samples to air dry in fume hood

Corrosion Testing

• Simulate physiological conditions

• Ringer’s solution:
  – Salts: NaCl, KCl, CaCl₂
  – pH ~ 7
  – T : 37 °C
  – t : 120 hr (5 days)
Characterization: Ellipsometry

• Polarized light is reflected from sample surface
• Polarization, incident and reflected angles, and light intensity are measured
• Material indices of refraction and absorbances are used to determine layer thickness
Characterization: SEM/EDS

- Scanning Electron Microscopy, Energy-Dispersive X-Ray Spectroscopy
- We can only indirectly detect dendrimers via C, N, and O on the surface of our devices
- Based on EDS intensities more dendrimers correspond to higher Cl concentration
- This supports our simulations showing ions trapped in the dendrimer layer
Characterization: ICP-OES

- Inductively Coupled Plasma Optical Emission Spectroscopy
- Solution is ionized, emitting a signature light spectra
  - Ppb resolution possible
- Quantitative data requires formation of a standard curve in appropriate matrix
• PAMAM monolayer decreases chloride ion diffusion into oxide by trapping the ions
• Ions diffuse into control oxide at a constant rate while ions cannot diffuse through dendrimers
• Overall: dendrimers can decrease pitting corrosion of titanium by trapping anions

Conclusion
Future Work

• Design Work
  – More iterations; better memory allocation

• Prototype Work
  – XPS characterization to quantitatively study Cl concentration after testing
  – EIS to study corrosion rate and possible pinholes
  – Study delamination; consider covalently bound dendrimers using polyethyleneglycol