Biomedical Implant Corrosion Passivation Using PAMAM Dendrimer Films

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OUTLINE

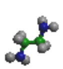
- *Background and Motivation*
- *Project Design Goals*
- *Technical Approach*
- *Modeling Results*
- *Prototyping*
- *Experimental Results*
- *Conclusion*

Background

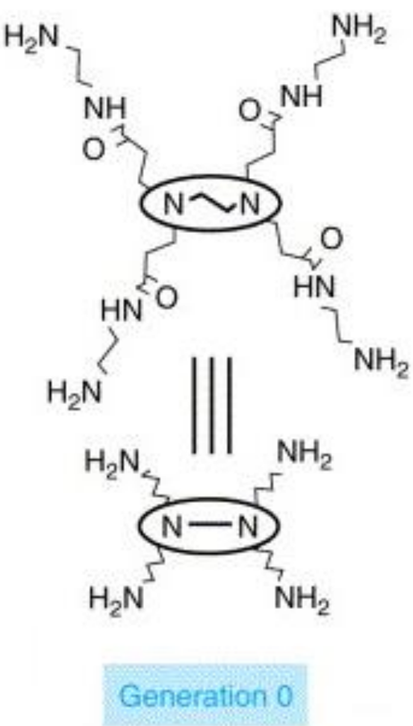
- Ti/TiO_2 is widely used for biomedical implants
- Passivation generally achieved by allowing the Ti to grow a native oxide layer
- Problem: oxide can corrode by pitting
  - Driven by concentration gradients of dissolved Cl^- and O_2
  - Pits expose reactive Ti metal below oxide

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

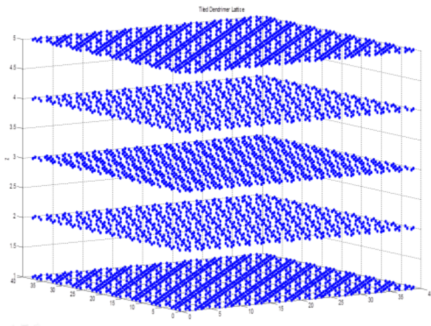
- Design a PAMAM dendrimer monolayer to passivate TiO_2 from pitting corrosion
- Model the diffusion of chloride ions in aqueous solution through PAMAM to TiO_2 surface using Kinetic Monte Carlo
- Investigate the diffusion of Ti ions from the sample through the dendrimer into a physiological solution

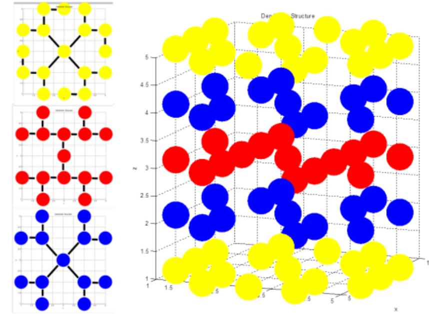
MODELING AND SIMULATIONS

- *Kinetic Monte Carlo Theory*
- *MATLAB Simulations*
- *Basic Approach*
- *Limitations*
- *Results*

Initial System

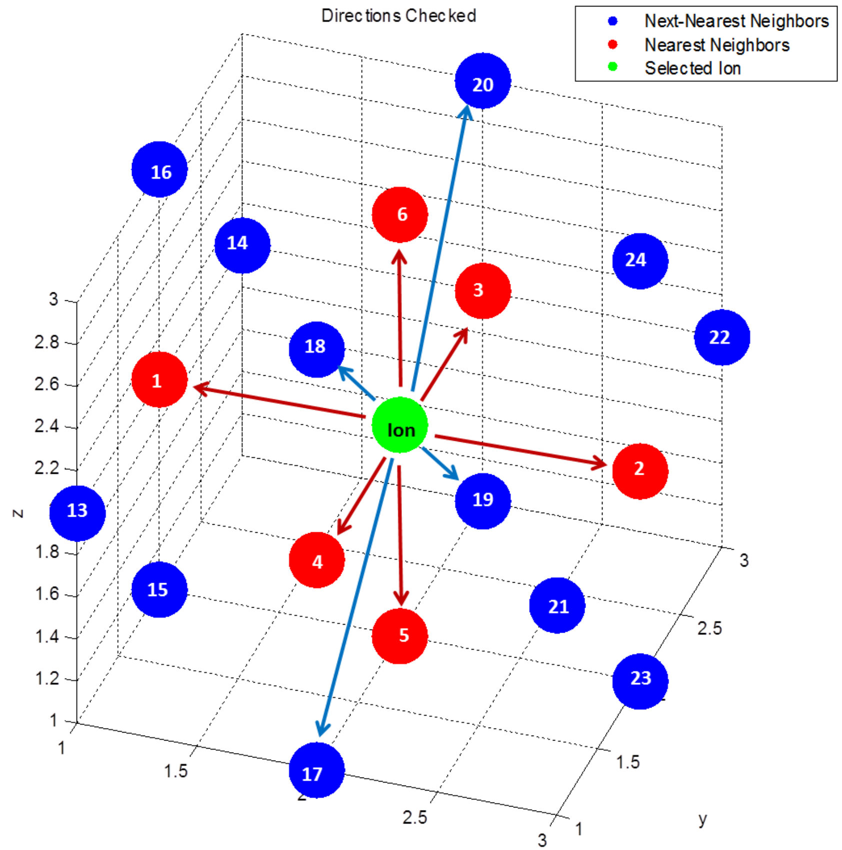
- Dendrimer film
  - Emulated by layered planes
  - Approximated as truncated cube
- Cl- ion solution
  - Random
- Total constraining volume
  - x*y*z 3D matrix
- Boundary constraints
  - No particles at system edge





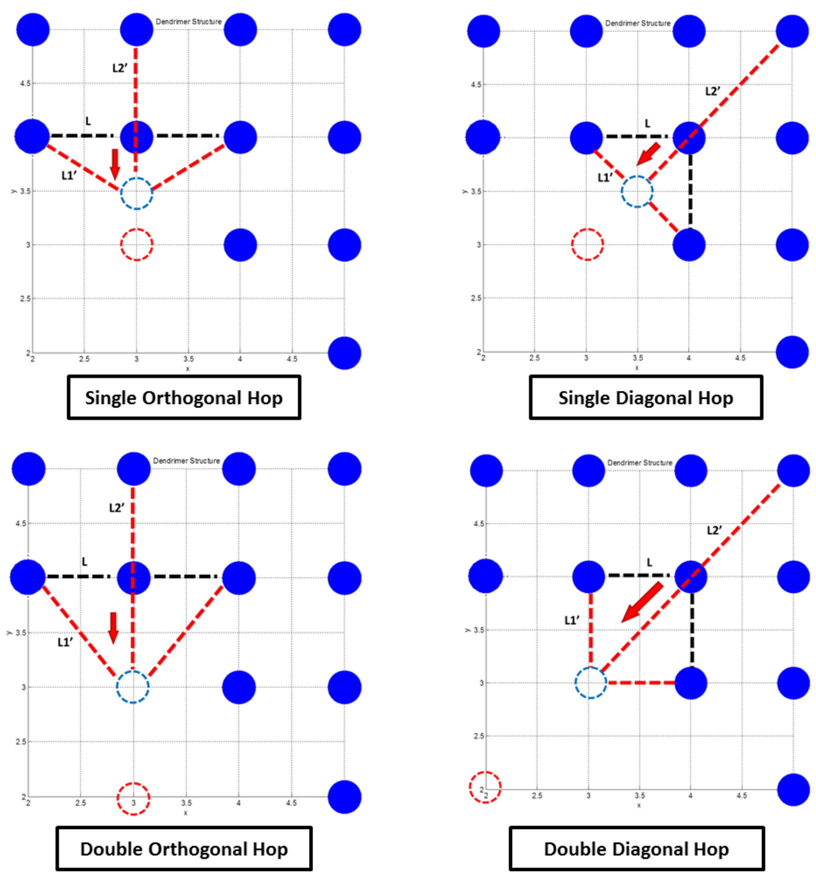
Directional Hopping Probability

- Two basic types: orthogonal and diagonal
  - 36 total possible directions defined
  - Single- and double-hops in each basic direction



Diagonal Hopping

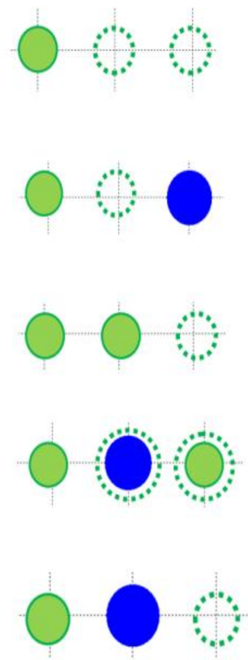
- Greater physical realism
- Hopping probabilities determined relative to orthogonal using geometric ratios and Hooke's Law



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 p1 and p2 :



$$\begin{bmatrix} right \\ right2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \qquad \begin{bmatrix} p1 \\ p2 \end{bmatrix} = \begin{bmatrix} pFluid \\ pFluid2 \end{bmatrix}$$

$$\begin{bmatrix} right \\ right2 \end{bmatrix} = \begin{bmatrix} 0 \\ n \end{bmatrix} \qquad \begin{bmatrix} p1 \\ p2 \end{bmatrix} = \begin{bmatrix} pFluid \\ 0 \end{bmatrix}$$

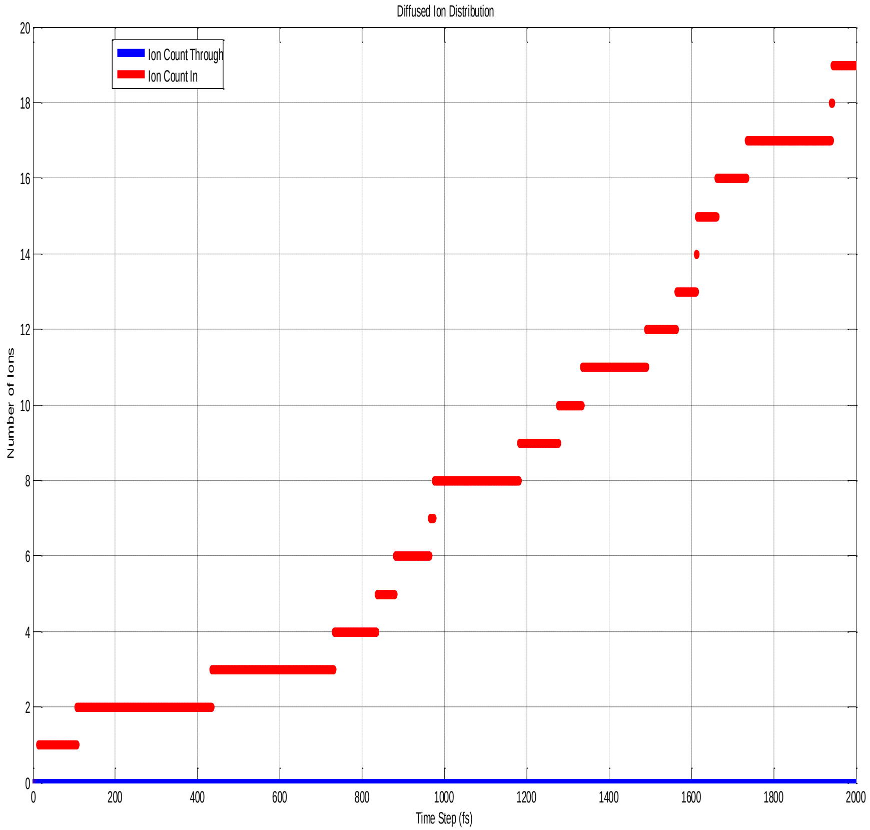
$$\begin{bmatrix} right \\ right2 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \begin{bmatrix} p1 \\ p2 \end{bmatrix} = \begin{bmatrix} 0 \\ pFluid2 \end{bmatrix}$$

$$\begin{bmatrix} right \\ right2 \end{bmatrix} = \begin{bmatrix} n \\ n \end{bmatrix} \qquad \begin{bmatrix} p1 \\ p2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} right \\ right2 \end{bmatrix} = \begin{bmatrix} 2 \\ 0 \end{bmatrix} \qquad \begin{bmatrix} p1 \\ p2 \end{bmatrix} = \begin{bmatrix} 0 \\ pBranch \end{bmatrix}$$

Diffusion Over Time

- 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

Comments

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

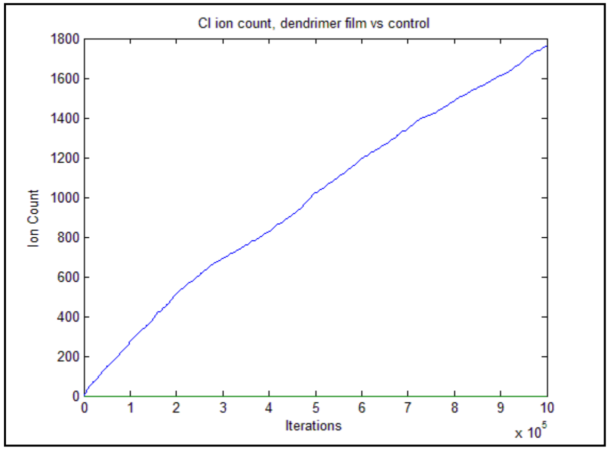
Results

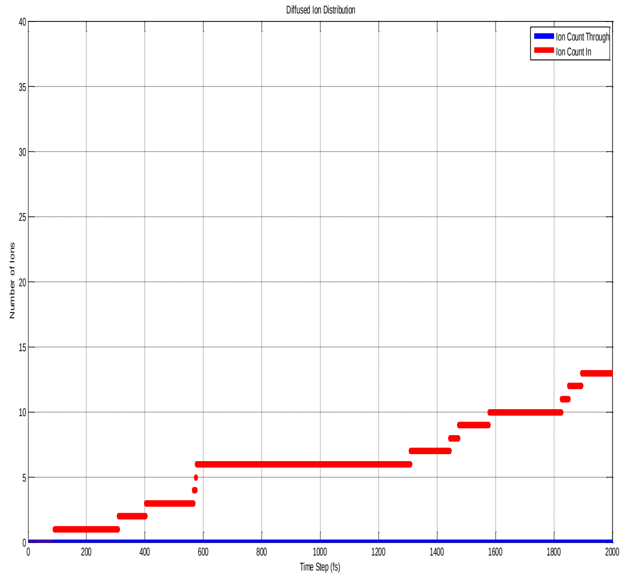
Control

- 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 O_2 gas at 700 ^oC for 1 hour
  - Plasma-enhanced: bombard samples with O_2 plasma at 400 ^oC for 2 minutes

Dendrimer Film Formation and Corrosion Testing

Fabrication procedure

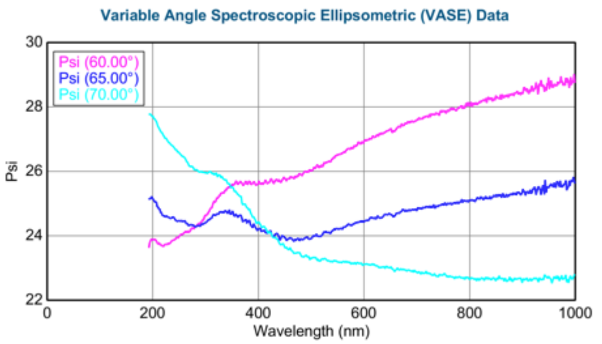
- 0.39 μm G5 PAMAM dendrimer in methanol
- Submerge titanium oxide surfaces in solution for 2 hours with agitation
- Allow samples to air dry in fume hood

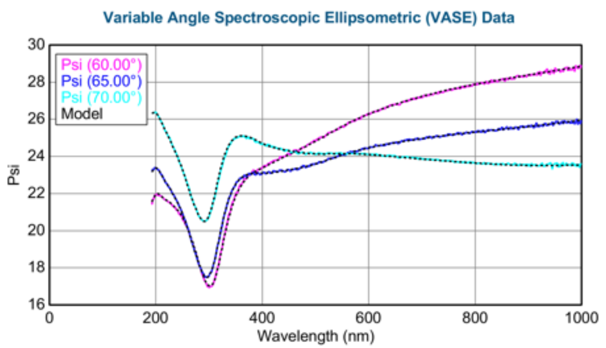
Corrosion Testing

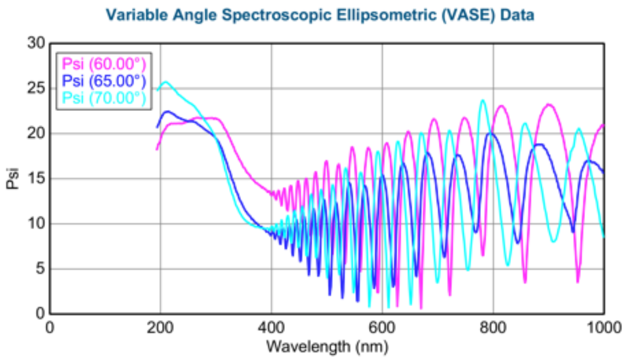
- Simulate physiological conditions
- Ringer's solution:
  - Salts: NaCl, KCl, $CaCl_2$
  - pH ~ 7
  - T : 37 ^{o}C
  - t : 120 hr (5 days)

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





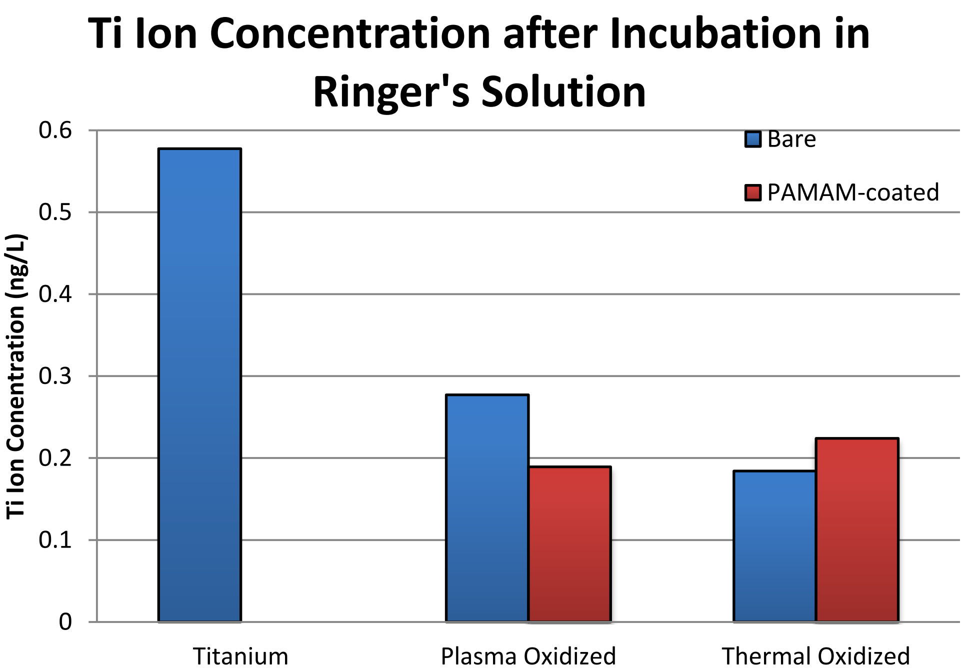


Characterization: SEM/EDS

- **S**canning **E**lectron **M**icroscopy, **E**nergy-**D**ispersive X-Ray **S**pectroscopy
- 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

- **I**nductively **C**oupled **P**lasma **O**ptical **E**mission **S**pectroscopy
- Solution is ionized, emitting a signature light spectra
  - Ppb resolution possible
- Quantitative data requires formation of a standard curve in appropriate matrix



Conclusion

- 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

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