MEMBRANE DEVELOPMENT FOR THE NEXT GENERATION OF CHEMICAL BIOLOGICAL PROTECTIVE CLOTHING

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Material Concept

Selectively Permeable Membrane

Perspiration Moisture Vapor

Agent Vapor

Liquid

Aerosols

Shell Fabric

Liner Fabric

Evaporative Cooling

Skin

Body
Vapor (V) Chemical Agent Protective Closure Systems
Vapor, Aerosol, Liquid, (VAL) Chemical, and Biological Agent Protective Closure Systems
All Purpose Personal Protective Ensemble (AP-PPE)

• Based on selectively permeable membranes
• Increased protection from liquids and aerosols
• Reduced weight and bulk
• Improved comfort and compatibility
• Improved operational suitability
• Reduced shelf-life burden
Membranes – Where do we go from here?

• Optimize permselectivity
• Ensure protection vs. toxic industrial chemicals (TICs)
• Introduce self-detoxification
• Integrate compatible closures
Ion Implanted Membranes

- Improve the permselectivity of membrane materials for use in chemical/biological (CB) protective clothing through the ion beam modification of the surface layers of available membranes.

- Two-fold approach: computer modeling of the irradiation process to develop a better understanding of the process at the molecular level and irradiation experiments of materials at different energy levels and with different ions for permselectivity measurements.

- Correlation between the two efforts will ultimately yield a powerful tool for the development of permselective membranes for CB garments.
Nafion® (du Pont): [\(-(\text{CF}_2\text{CF}_2)\text{n}-(\text{CF}_2\text{CF}(\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}))\text{)}\text{]}\text{x} \]

Schematic model of Nafion: hydrophilic, intermediate and hydrophobic phases
Transport of Ions in Matter (SRIM v.2000.41 )¹

Depth vs. Y-Axis

Example of simulation profiles

- S damage
- F damage
- Sidechain damage
- Backbone damage
- Implanted ions

Damage event, per corresponding target atom

Implant event, per 10,000 substrate atom

Depth (µm)
Implant ion stopping in Nafion®

Projectile ion
- S+
- F+
- O+
- N+
- C+
- He+
- H+
- Fit

\[ \lg \left( \frac{R}{\mu m} \right) = 0.857 \cdot \lg \left( \frac{E}{\text{keV}} / Z_1 \right) - 1.543 \]

\( r^2 = 0.985 \), \( F = 2142 \) d.f. 33
Surface analysis: $C_{1s}$ XPS spectra of pristine and ion beam damaged Nafion®

a.) Pristine

Hydrocarbon contamination

b.) F+ implanted

beta-shifted

c.) N+ implanted

graphitic
Water Permeation in NAFION 117

- **Untreated**
- **Nitrogen Implanted, 1.0e15 ions/cm²**
- **Fluorine Implanted, 1.0e15 ions/cm²**

Flux (g/day/m²) vs. Time (min)
N-propanol Permeation in NAFION 117

untreated

nitrogen implanted, 5.0e13 ions/cm²
Protolyte A700

Flux (g/d/m²) vs. Time (min)

- Untreated, 80% water
- 1e14 N, 80% water
Protolyte A700

Flux (g/d/m²)

Time (min)

- Untreated, 80% n-prop
- 1e14 N, 80% n-prop
- Untreated, 40% TCE
- 1e14 N, 40% TCE
Summary – Ion Implantation

• Medium-energy ion beam treatment is a promising technique for developing barrier membranes selectively permeable to water vapor.

• Theoretical calculations are a useful adjunct for optimizing treatment conditions.

• XPS measurements of the surface reveal that ion bombardment leads to loss of fluorine, with the eventual formation of a carbonized layer.

• This two-pronged approach will ultimately yield a powerful technique for the development of permselective membranes for CB protective garments.
Perforated Monolayer Approach

Assembly of Molecular Pores

Porous Molecule

Small Gas Molecule

Large Gas Molecule
The Langmuir-Blodgett Method

A stylized illustration showing a single surfactant monolayer being transferred to a hydrophobic support on a down-trip, followed by the transfer of a second monolayer on the up-trip, to form a bilayer.
Perforated Monolayers

An illustration of a perforated monolayer formed from a porous surfactant.
Space filling models of an analog of II

Side View

Top View
Composite membrane formed from a bilayer of $\text{II}$ and poly[1-(trimethylsilyl)-1-propyne] (PTMSP)
Perforated Monolayer of II

\[ \alpha_{\text{He/N}_2} = 18 \]
Improved Perforated Monolayers through “Gluing”

• Ionic cross-linking of a cationic calix[6]arene-based LB film by use of a water-soluble polyanion, would produce a two-dimensional network with enhanced stability

• Filling in void space (defects), the polymeric counterion would result in enhanced permeation selectivity
An illustration of a LB bilayer, made from a multiply charged calix[6]arene that has been glued together through the use of a polymeric counterion.
Perforated Monolayer of III & PSS

\[ \alpha_{\text{He/N}_2} = 240 \]
microporous PTFE

The diagram shows the time (min) on the x-axis and a variable on the y-axis. The graph includes data points for 100% RH, 80% RH, 60% RH, 40% RH, and 20% RH, with different markers for each RH level.
Summary – Monolayers

• The surface modification of organic polymers by a tightly packed monolayer of calix[6]arenes or other surfactants could constitute an attractive, selectively permeable barrier, allowing the passage of water vapor (perspiration), while serving as a barrier to chemical warfare agents.
• Due to its ultrathin and microporous structure, it is expected that the flux of water across such a membrane would be maximized.
• The composite membranes could be used in the protective layer of the next generation of chemical protective clothing.
• These novel clothing ensembles would potentially be dramatically lighter weight than current systems.
Summary/Challenges
Clothing Operational Context

- Improved system integration with suit, mask, helmet, gloves, boots, body armor, weapons, etc. (JSLIST Upgrade)
- Reactive clothing materials with increased protection, reduced doffing hazard, and reduced logistics burden. (JSLIST Upgrade)
- Cool, lightweight CB duty uniform based on nanofiber or membrane technology with increased mission duration and a reduced logistics burden. (JSLIST Upgrade)