Transport Measurement and Modeling for Assessment of Coating System Performance

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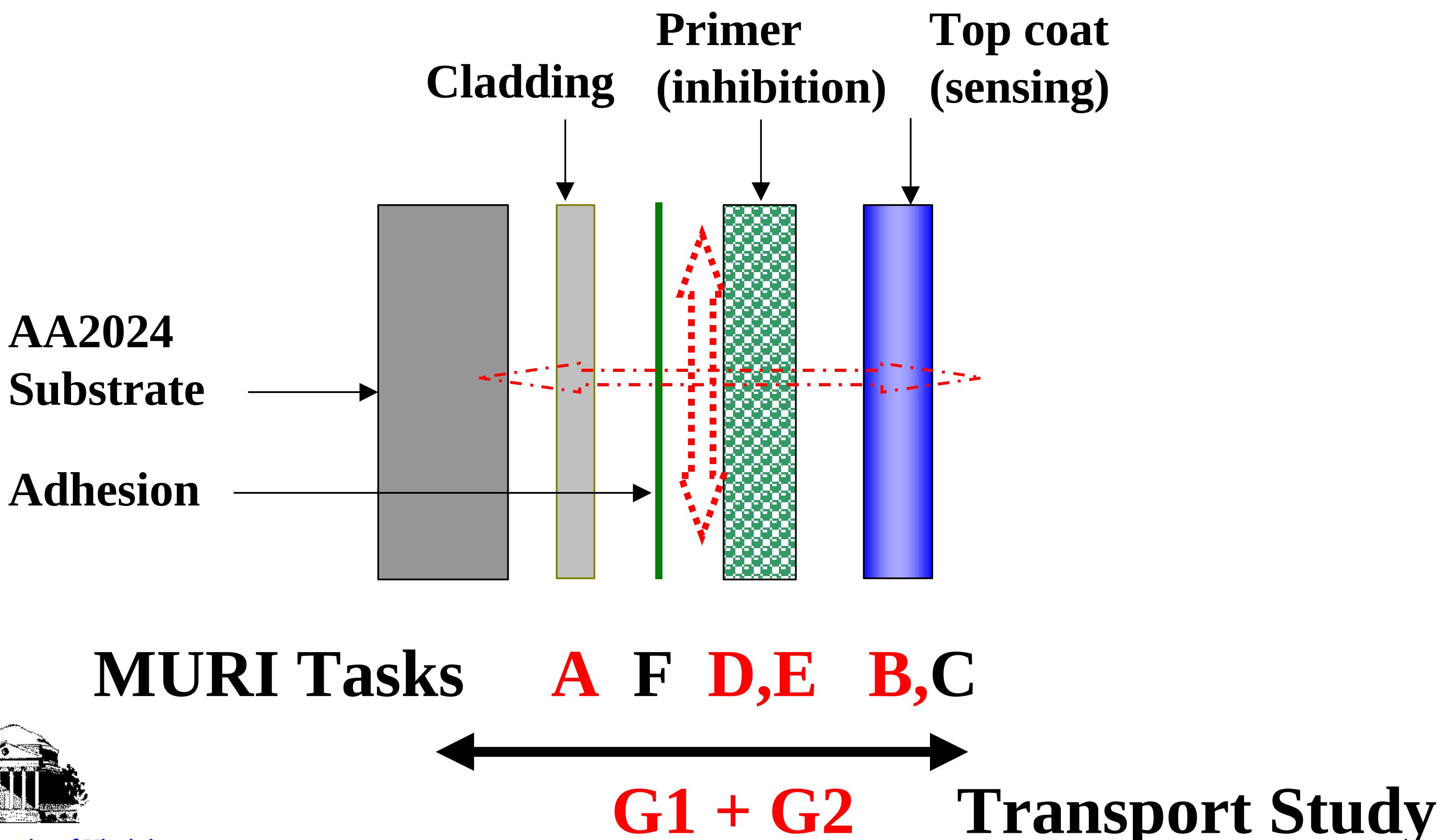
Introduction



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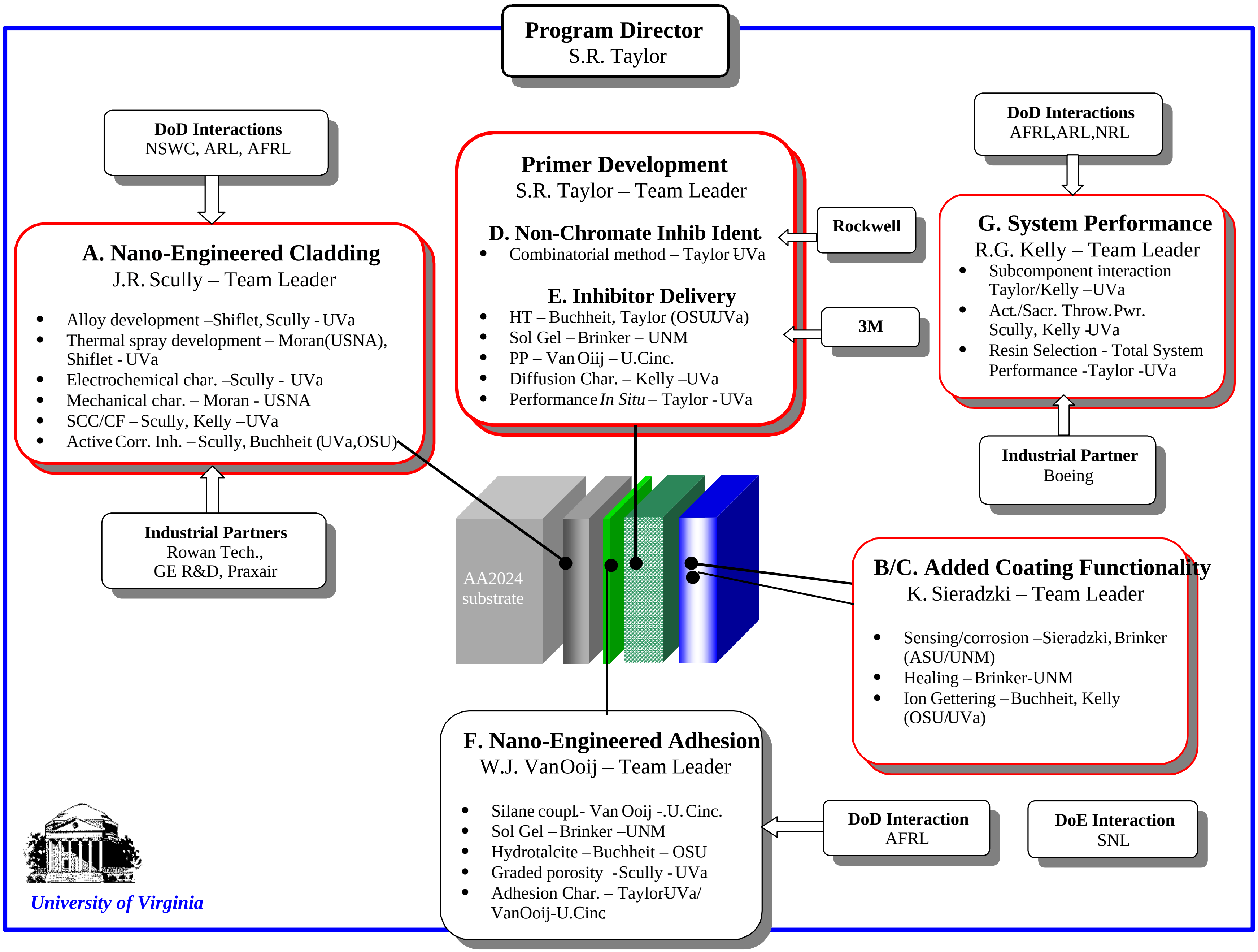
Program Director
S.R. Taylor
DoD Interactions
NSWC, ARL, AFRL
A. Nano-Engineered Cladding
J.R. Scully – Team Leader
• Alloy development – Shiflet, Scully - UVa
• Thermal spray development – Moran (USNA), Shiflet - UVa
• Electrochemical char. – Scully - UVa
• Mechanical char. – Moran - USNA
• SCC/CF – Scully, Kelly – UVa
• Active Corr. Inh. – Scully, Buchheit (UVa, OSU)
Industrial Partners
Rowan Tech.,
GE R&D, Praxair
Primer Development
S.R. Taylor – Team Leader
D. Non-Chromate Inhib Ident.
• Combinatorial method – Taylor UVa
E. Inhibitor Delivery
• HT – Buchheit, Taylor (OSU/UVa)
• Sol Gel – Brinker – UNM
• PP – Van Oiij – U.Cinc.
• Diffusion Char. – Kelly – UVa
• Performance *In Situ* – Taylor - UVa
Rockwell
3M
DoD Interactions
AFRL, ARL, NRL
G. System Performance
R.G. Kelly – Team Leader
• Subcomponent interaction Taylor/Kelly – UVa
• Act./Sacr. Throw. Pwr. Scully, Kelly - UVa
• Resin Selection - Total System Performance - Taylor - UVa
Industrial Partner
Boeing
AA2024
substrate
B/C. Added Coating Functionality
K. Sieradzki – Team Leader
• Sensing/corrosion – Sieradzki, Brinker (ASU/UNM)
• Healing – Brinker-UNM
• Ion Gettering – Buchheit, Kelly (OSU/UVa)
F. Nano-Engineered Adhesion
W.J. VanOoij – Team Leader
• Silane coupl. - Van Ooij - U. Cinc.
• Sol Gel – Brinker – UNM
• Hydrotalcite – Buchheit – OSU
• Graded porosity - Scully - UVa
• Adhesion Char. – Taylor-UVa/ VanOoij-U.Cinc
DoD Interaction
AFRL
DoE Interaction
SNL
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Goals of Transport Studies

Assistance to other tasks in determination of movement of species by mass transport

- Experimental
  - Measurements of leaching rates of inhibitors or other agents under range of conditions
  - Interpretation in terms of structure-composition-property
- Computational
  - Mechanism-based modeling
  - Test expected dependencies of release and transport

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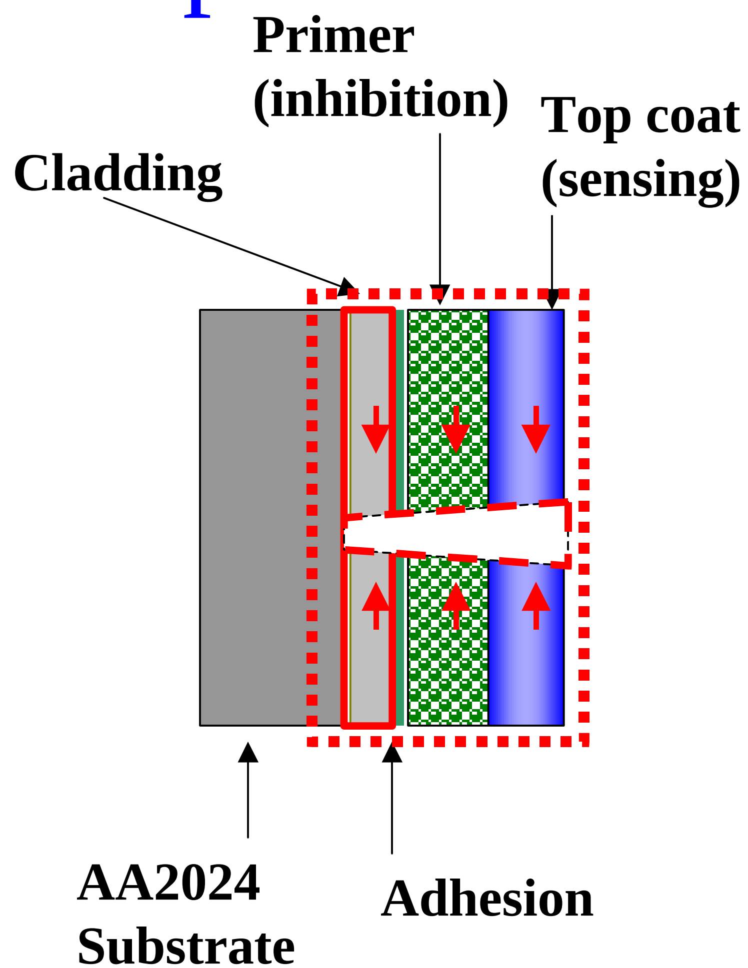
Transport Challenges

- Accuracy of computational model depends on the underlying assumptions and quality of parameter values
  - Understanding phenomena governing transport
  - Measuring relevant transport parameters
- In-situ microscopy provides detailed information on mass transfer at the micro-level
- Experimental and modeling efforts bridge the gap between microscopic and macroscopic approaches

Scenarios and Transport Models

- **Bulk transport & release of species**
  - **Top coat**
  - **Primer**
  - **Cladding**
- **Solution chemistry transport**
  - **At defects**
- **Electrochemical effects**
  - **Cladding throwing power**



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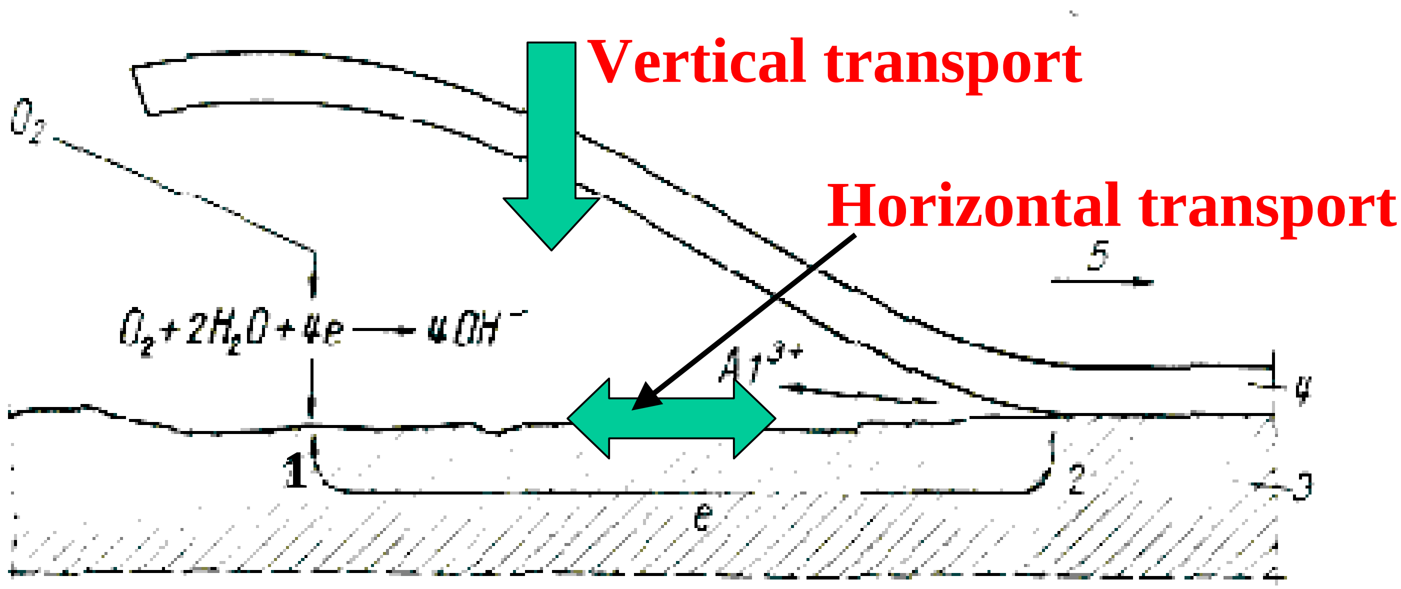
Blister Modeling



Schematic of the mechanism of anodic undermining reproduced from de Jong et al. (1986). A thin layer of substrate is dissolved, leading to coating detachment. Note the (1) locations of the cathode and (2) the anode. (3) represents the substrate, (4) corresponds to the coating, and (5) indicates the direction of blister growth.

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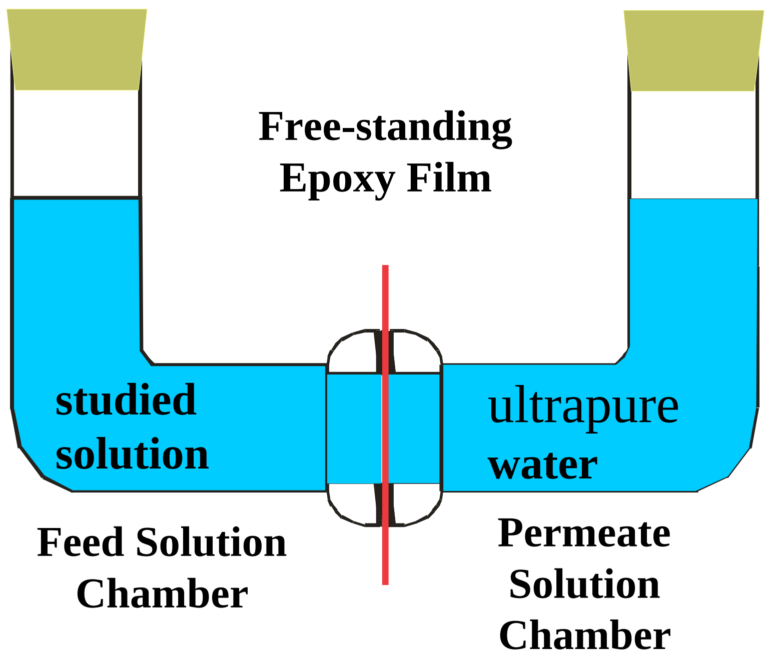
Transport Review
Modeling

- Blistering growth mechanism and modeling
  - Framework in aluminum alloy coating system (Schneider, Williams, Kelly, 2001)
  - Growth modeling for steel-coating system (Nguyen et al., 1997)
- Disbonded coating with cathodic protection
  - Reactive transport modeling using finite element method (Sridhar et al., 2001)
- Will extend UVa crevice mass transport model to coating components and system

Transport Review
Measurements

- Uptake of water into epoxy films (Williams et al., 2001)
  - Lower ionic concentrations lead to higher water uptake
- Transport through conducting polymer composite membranes (Davey et al., 2001)
  - Sequence flux $K^{+} > Na^{+} > Ca^{2+} > Mg^{2+}$, related to the hydration of cation
- Transport in tumor control (Jain, 1994)
  - Improve drug delivery (*i.e.*, macromolecules)

Preliminary Ionic Transport Measurements



- Withdraw 20 μL solution samples from permeate solution chamber regularly; Fill the permeate chamber with 20 μL ultrapure water;

- Detect the concentrations of different ions by CE;

- Record the concentration-time data;

- Calculate apparent diffusion coefficients of chemical species;

- Compare the effects of different parameters.

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Analysis Procedure

- Measurement by Capillary Electrophoresis
- $D = \boldsymbol{b}\, VT/(C_0A)$

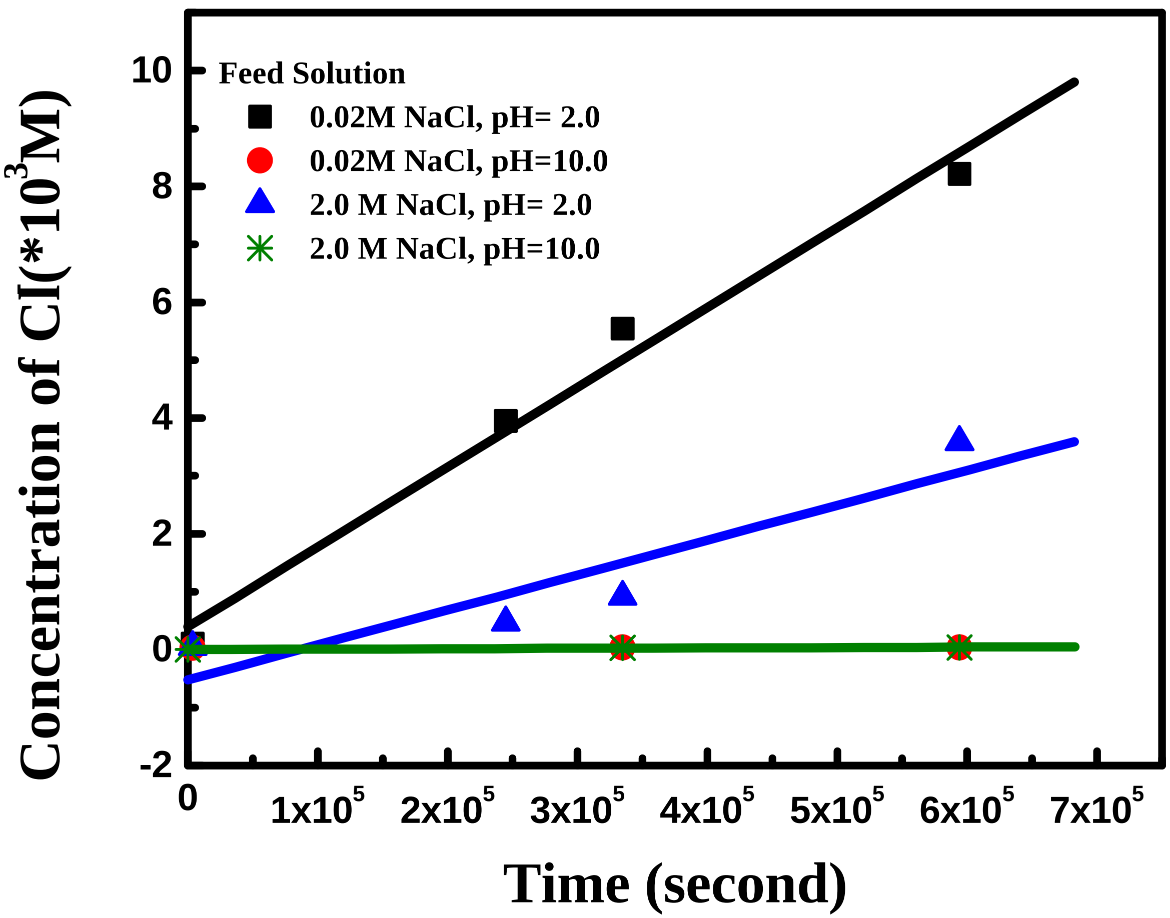
b —— the steady state ion flux, *i.e.*, the slope of the concentration vs. time curve obtained by curve fitting to experimental data.

V —— the volume of the half cell.

T —— the thickness of epoxy film.

C_0—— the concentration of the feed ion solution.

A —— the area of the film exposed to the solutions.



Transport of Cl^- from feed chamber to permeate chamber across free-standing epoxy films using NaCl solution

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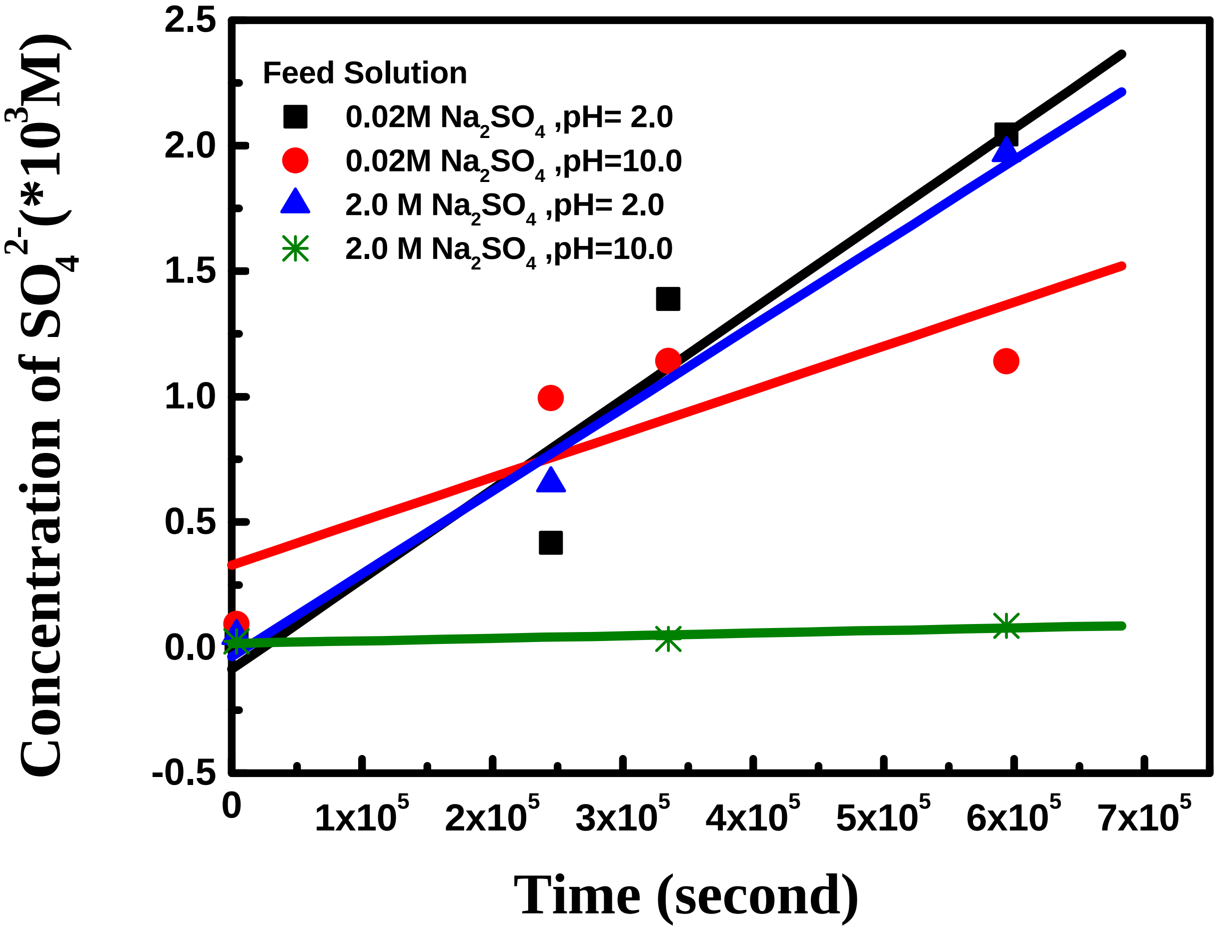

Transport of SO_4^{2-} from feed chamber to permeate chamber across epoxy freestanding films using Na_2SO_4 solution

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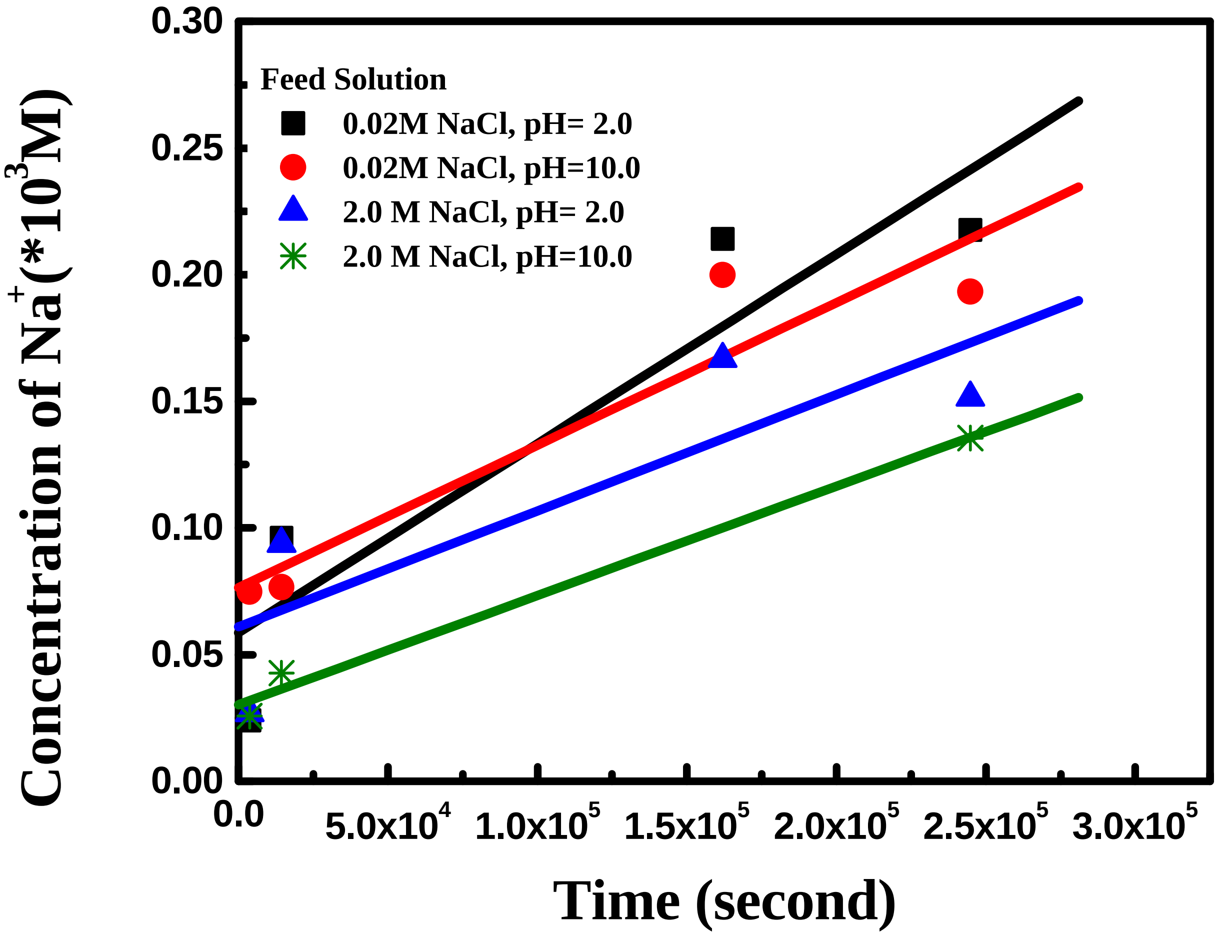

Transport of Na^+ from feed chamber to permeate chamber across epoxy freestanding films using NaCl solution

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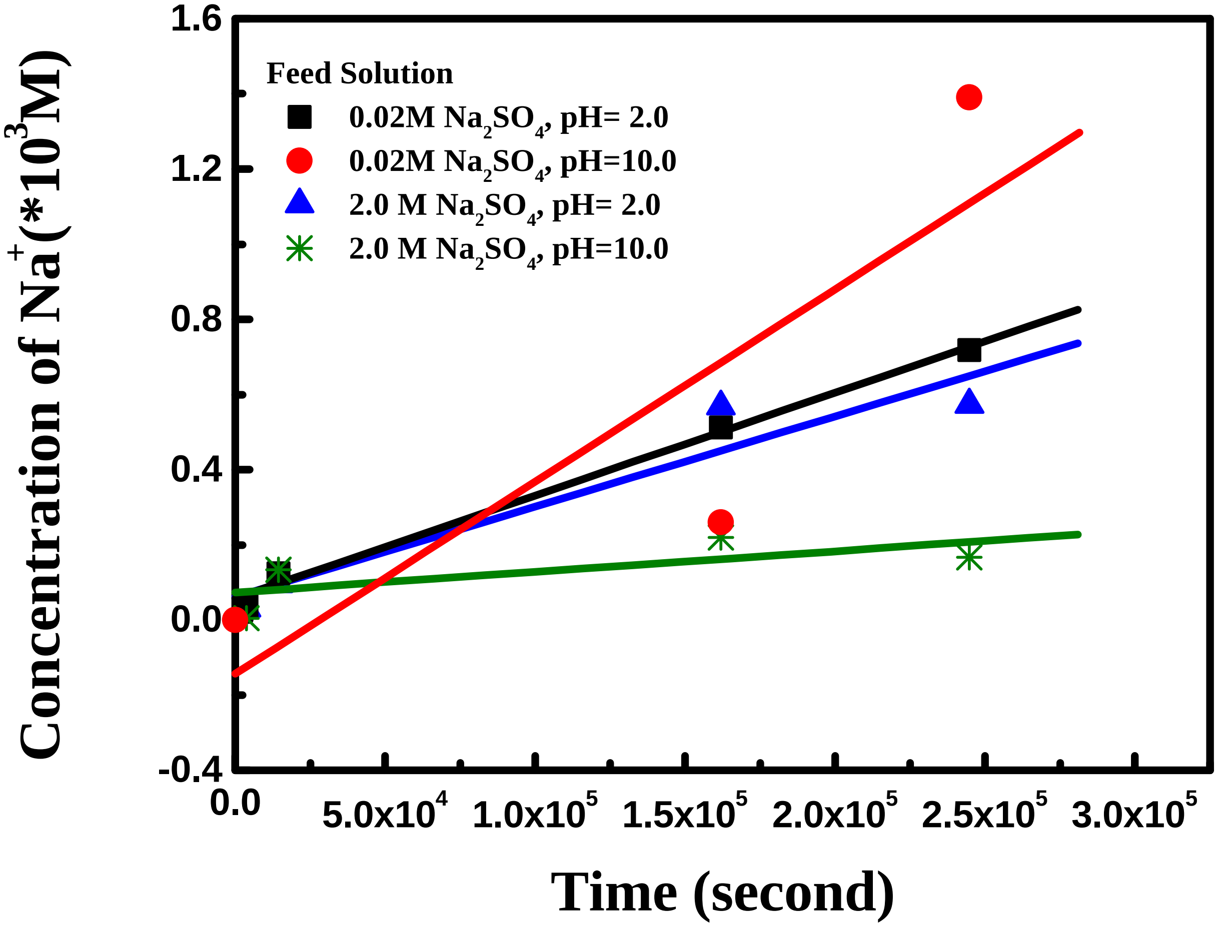

Transport of Na^+ from feed chamber to permeate chamber across epoxy freestanding films using Na_2SO_4 solution

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Chloride Transport

pH, Concentration Effects

Feed Solution	$D_{Chloride}$(cm^2/sec)	R^2
0.02M NaCl, pH=2.0	$4.1*10^{-9}$	0.99
0.02M NaCl, pH=10.0	$2.0*10^{-12}$	0.99
2.0M NaCl, pH=2.0	$1.7*10^{-11}$	0.85
2.0M NaCl, pH=10.0	$2*10^{-13}$	0.93

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Sulfate Transport

pH, Concentration Effects

Feed Solution	$D_{sulfate}(cm^2/sec)$	R^2
0.02M Na_2SO_4, pH=2.0	$1*10^{-9}$	0.91
0.02M Na_2SO_4, pH=10.0	$5.1*10^{-10}$	0.71
2.0M Na_2SO_4, pH=2.0	$9.7*10^{-12}$	0.99
2.0M Na_2SO_4, pH=10.0	$3.0*10^{-13}$	0.82

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Sodium Transport

pH, Concentration Effects

Feed Solution	D_{sodium} (cm^2/sec)	R^2
0.02M NaCl, pH=2.0	$2.2*10^{-10}$	0.86
0.02M NaCl, pH=10.0	$1.6*10^{-10}$	0.89
2.0M NaCl, pH=2.0	$1.4*10^{-12}$	0.72
2.0M NaCl, pH=10.0	$1.3*10^{-12}$	0.99
0.02M Na_2SO_4, pH=2.0	$3.5*10^{-10}$	0.92
0.02M Na_2SO_4, pH=10.0	$7.5*10^{-10}$	0.74
2.0M Na_2SO_4, pH=2.0	$4.0*10^{-12}$	0.99
2.0M Na_2SO_4, pH=10.0	$8.1*10^{-13}$	0.50

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Conclusions to Date

- Anions (Cl^-, SO_4^{2-}) transport in film
  - – Lower concentrations in feed solution lead to higher apparent diffusivity
    - Due to higher water uptake
  - – Lower pH leads to higher apparent diffusivity
    - Due to film damage
- Cation (Na^+) transport in film
  - – Lower concentrations lead to higher apparent diffusivity
  - – No effect of pH on transport (scatter in measurements)

Future Work

- Experiment
  - **Continue the current work**
  - Extend to release & transport of inhibitors and other species in MURI Tasks
- Modeling
  - **Make flexible model for individual layers**
  - **Throwing power computational modeling**
  - Total coating system evaluation

Acknowledgments

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