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5c. PROGRAM ELEMENT NUMBER
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6. AUTHORS

5d. PROJECT NUMBER

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5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Connecticut - Storrs
Sponsored Program Services
438 Whitney Road Ext., Unit 1133
Storrs, CT 06269 -1133

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14. ABSTRACT

15. SUBJECT TERMS

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Wilson Chiu
UU	UU	UU	UU		19b. TELEPHONE NUMBER 860-486-3647

RPPR Final Report
as of 26-Dec-2018

Agency Code:

Proposal Number: 63055CH **Agreement Number: W911NF-14-1-0298**
INVESTIGATOR(S):

Name: Ph.D Wilson K. S. Chiu
Email: wchiu@engr.uconn.edu
Phone Number: 8604863647
Principal: Y

Organization: **University of Connecticut - Storrs**
Address: Sponsored Program Services, Storrs, CT 062691133
Country: USA
DUNS Number: 614209054 EIN: 060772160
Report Date: 30-Nov-2018 Date Received: 09-Dec-2018
Final Report for Period Beginning 23-Jun-2014 and Ending 31-Aug-2018
Title: Carbonate and Hydroxide Ion Transport in Alkaline Anion Exchange Materials
Begin Performance Period: 23-Jun-2014 **End Performance Period:** 31-Aug-2018
Report Term: 0-Other
Submitted By: Ph.D Wilson Chiu Email: wchiu@engr.uconn.edu
Phone: (860) 486-3647

STEM Degrees: 4 **STEM Participants:** 5

Major Goals: Objective
Even though there is significantly greater understanding of the proton transport mechanism in the cation exchange membranes, the dominant carbonate and OH- ion transport mechanisms in the anion exchange membrane (AEM) are yet unclear. Preliminary results have shown that we can successfully predict OH- conductivity, ion dissociation processes, and water flux in the AEM This project will obtain fundamental understanding into the formation and transport of carbonate ions and hydroxide ions in AEM material, and then to examine solutions for AEM stability and performance in the presence of carbon dioxide.

Approach
A detailed understanding of how carbonate ions and hydroxide ions form and transport in AEM material is needed in order to understand how they affect the ionic conductivity and stability of the AEM material. This will be achieved by creating analytical/numerical models to accurately describe the formation and transport of carbonate ions and hydroxide ions in the AEM, validating the model using experimental data obtained provided by our collaborators at the Army Research Laboratory (Dr. Deryn Chu, Dr. Kyle Grew, and Dr. Xiaoming Ren), Vanderbilt University (Prof. Peter Pintauro), and from the published literature, and exploring solutions for AEM stability and performance in the presence of carbon dioxide.

Relevance to the Army
There are considerable Army power and energy needs including Soldier & Sensor power, Field/Base power, Vehicle power and Air Platform power. The Army has targeted fuel cells as a candidate for portable power, APUs, UAV/UGV, and unattended ground sensors. Applications include methanol-fueled fuel cells for Future Warriors (72 hour mission), and logistic-fueled fuel cells for 96 hour missions. There is significant interest in alkaline fuel cells utilizing solid-polymer alkaline anion exchange membranes (AEM), which are the high pH equivalent to proton exchange membranes (e.g. Nafion). The alkaline membrane fuel cell (AMFC) provide opportunities for the direct use of alcohol fuels. As detailed in the Army Research Office 2011 Alkaline Membrane Fuel Cell Workshop Final Report, the AMFC is seen as a promising candidate for high energy density portable power applications, and specifically those in the vicinity of 20-100 W with some unique opportunities for small passive devices in the 1-5 W range.

Accomplishments: Accomplishments
This project has achieved several major accomplishments:
- Used analytical Effective Media Theory to successfully estimate the electrospun AEM's hydroxide conductivity.
- Performed a collaborative study with ARL to investigate the effect of CO2 on Nafion material.

- Obtained fundamental understanding into the transient formation and transport of carbonate ions and hydroxide ions in AEM material in the presence of CO2.
- Created Fiber Network (FN) ion transport model to simulate the three-dimensional fibrous microstructural morphology and predict properties that result from the electrospinning membrane fabrication process.
- Examined the effect of CO2 on cast and electrospun AEM.
- Identified potential CO2 mitigation strategies, e.g. self-purging, electrospinning.
- Created a fully analytical Analytical Transport Network Model to explicitly relate a microstructural network's topology and the morphology of its channels to an effective material transport coefficient with computational time that is 5–6 orders of magnitude faster than finite element analysis.

Training Opportunities: Personnel Involved in this Project

- Jacob A. Wrubel, Ph.D. candidate, expected May, 2019
- Peter J. Damian, M.S., December, 2018
- Alex P. Cocco, Ph.D., December, 2016
- Matthew B. DeGostin, M.S., August 2015
- Timothy D. Myles, Ph.D., December, 2014

RPPR Final Report
as of 26-Dec-2018

Results Dissemination: Resulting Journal Publications

1. Papers Published in Peer-Reviewed Journals (8)

1. A. P. Cocco, A. Nakajo, and W. K. S. Chiu, “Analytical Transport Network Theory to Guide the Design of 3-D Microstructural Networks in Energy Materials: Part 1. Flow without Reactions,” J. Power Sources, 372: 297-311, 2018.
2. A. P. Cocco and W. K. S. Chiu, “Analytical Transport Network Theory to Guide the Design of 3-D Microstructural Networks in Energy Materials: Part 2. Flow with Reactions,” J. Power Sources, 372: 312-324, 2018.
3. J. A. Wrubel, A. A. Peracchio, B. N. Cassenti, T. D. Myles, K. N. Grew, and W. K. S. Chiu, “Anion Exchange Membrane Ionic Conductivity in the Presence of Carbon Dioxide under Fuel Cell Operating Conditions,” J. Electrochem. Soc., 164(12): F1-F11, 2017.
4. M. B. DeGostin, A. A. Peracchio, T. D. Myles, B. N. Cassenti, and W. K. S. Chiu, “Charge Transport in the Electrospun Nanofiber Composite Membrane’s Three-Dimensional Fibrous Structure,” J. Power Sources, 307: 538-551, 2016.
5. X. Ren, T. D. Myles, K. N. Grew, and W. K. S. Chiu, “Carbon Dioxide Transport in Nafion 1100 EW Membrane and in a Direct Methanol Fuel Cell,” J. Electrochem. Soc., 162: F1221-F1230, 2015.
6. T. D. Myles, K. N. Grew, A. A. Peracchio, and W. K. S. Chiu, “Transient Ion Exchange of Anion Exchange Membranes Exposed to Carbon Dioxide,” J. Power Sources, 296: 225-236, 2015.
7. T. D. Myles, A. A. Peracchio, and W. K. S. Chiu, “Extension of Anisotropic Effective Medium Theory to Account for an Arbitrary Number of Inclusion Types,” J. Appl. Phys., 117: 025101, 2015.
8. T. D. Myles, A. A. Peracchio, U. Pasaogullari, and W. K. S. Chiu, “Application of a New Effective Medium Formulation to Account for Transport due to Fiber and Web-like Inclusions in Gas Diffusion Layers,” J. Electrochem. Soc., 162: F645-F650, 2015.

2. Manuscripts to be Submitted (2)

1. J. A. Wrubel, A. J. Peracchio, B. N Cassenti, K. N. Grew, and W. K. S. Chiu, “Anion Exchange Membrane Fuel Cell Performance in the presence of Carbon Dioxide: An Investigation into the Self-Purging Mechanism,” to be submitted, 2018.
2. J. A. Wrubel, A. A. Peracchio, B. N. Cassenti, T. J. Omasta, W. E. Mustain, K. N. Grew and W. K. S. Chiu, “Effects of Carbon Dioxide on the Conductivity of Electrospun and Radiation-Grafted Anion Exchange Membranes,” to be submitted, 2018.

3. Conference Proceedings, Presentations and Abstracts (4)

1. J. A. Wrubel, A. J. Peracchio, B. N. Cassenti, K. N. Grew and W. K. S. Chiu, “Predicting Electrospun Anion Exchange Membrane Conductivity in the Presence of Carbon Dioxide,” 233rd Electrochemical Society Meeting, Abstract No. 108354, Seattle, WA, May 13-27, 2018.
2. A. P. Cocco, A. Nakajo, K. N. Grew and W. K. S. Chiu, “The Analytical Transport Network Model for Diffusive-Reactive Flow in 3-D Microstructural Networks: A Computationally Economical Model for Potential Use in Multi-Scale Modeling Efforts,” 233rd Electrochemical Society Meeting, Abstract No. 108886, Seattle, WA, May 13-27, 2018.
3. J. A. Wrubel, A. J. Peracchio, B. N. Cassenti, T. D. Myles, K. N. Grew and W. K. S. Chiu, “Anion Exchange Membrane Ionic Conductivity in the Presence of Carbon Dioxide under Fuel Cell Operating Conditions,” 232nd Electrochemical Society Meeting, Abstract No. 105132, National Harbor, MD, October 1-6, 2017 (ECS Trans., 80, 2017).
4. A. P. Cocco, A. Nakajo, K. N. Grew and W. K. S. Chiu, “Analytical Models for Diffusive-Reactive Flow in 3-D Microstructural Networks to Guide the Design of Electrochemical Materials,” 232nd Electrochemical Society Meeting, Abstract No. 104760, National Harbor, MD, October 1-6, 2017.

RPPR Final Report
as of 26-Dec-2018

Honors and Awards: Awards, Honors and Appointments

Alex P. Cocco
o Postdoctoral Fellow, Army Research Laboratory, Adelphi, MD.

Wilson K. S. Chiu
Editorial Activities
o Editor, ASME Journal of Electrochemical Energy Conversion and Storage, 2016-2020.
o Editorial Board, Scientific Reports, Nature Publishing Group, since 2015.
Advisory Boards / Review Committees
o NSLS-II Microscopy and Imaging Proposal Review Panel, National Synchrotron Light Source II, Brookhaven National Laboratory, NY, 2017 – 2020.
o NSLS-II Science Advisory Committee (SAC) Review Committee, HXN Triennial Beamline Review, National Synchrotron Light Source II, Brookhaven National Laboratory, NY, 2018.
o Full field X-ray Imaging (FXI) Beamline Advisory Team, National Synchrotron Light Source II, Brookhaven National Laboratory, NY, 2012 – 2017 (Chair, 2017).
o Imaging Beam Line Review Committee, Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Stanford, CA, 2015.
Keynote/Invited Speaker:
o Invited Speaker, Army Research Laboratory, Adelphi, MD, September 18, 2018.
o Invited Speaker, Focused Session on Materials Issues in Nuclear Waste Treatment and Disposal, 8th Forum on New Materials, 14th International Conference on Modern Materials and Technologies (CIMTEC 2018), Perugia, Italy, June 10-14, 2018.
o Invited Department Seminar Speaker, University of California, Irvine, Department of Mechanical and Aerospace Engineering, Irvine, CA, June 1, 2018.
o Invited Department Seminar Speaker, Technical University of Denmark, Department of Energy Conversion and Storage, Riso, Denmark, November 14, 2017.
o Invited Department Seminar Speaker, Clemson University, Department of Materials Science and Engineering, Clemson, SC, September 14, 2017.
o Invited Speaker, OFS Specialty Photonics Division, Avon, CT, July 14, 2017.
o Keynote Speaker, 7th International Symposium on Advances in Computational Heat Transfer (CHT-17), Naples, Italy, May 28-June 1, 2017.
o Invited Speaker, IEK-1 Materials Synthesis and Processing, Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH, Jülich, Germany, September 22, 2016.
o Invited Speaker, Indo-US Science and Technology Forum on Recent Advances in Multiscale, Multiphysics Analysis of Energy Conversion in Li-Ion Batteries, Mumbai, India, June 17-19, 2016.
o Invited Speaker, 12th International Conference on Durability of Composite Systems (DURACOSYS), Arlington, TX, June 12-15, 2016.
o Invited Speaker, Photon Science Seminar Series, SLAC National Accelerator Laboratory, Stanford, CA, May 25, 2016.
o Invited Department Seminar Speaker, EPFL Valais-Wallis, Sion, Switzerland, March 24, 2016.
o Keynote Speaker, 13th Symposium on Modeling & Experimental Validation of Fuel Cells, Batteries & Electrolysers (MODVAL13), Lausanne, Switzerland, March 22-23, 2016.
o Invited Speaker, TMS 2016 145th Annual Meeting & Exhibition, Nashville, TN, February 15, 2016.
o Keynote Speaker, International Conference on Computational & Experimental Engineering and Sciences (ICCES'15), Reno, NV, July 23, 2015.
o Invited Speaker, Duracell Technical Center, Berkshire Corporate Park, Bethel, CT, Monday, June 8, 2015.
o Invited Speaker, 6th International Symposium on Computational Heat Transfer (CHT-15), Rutgers University, Piscataway, NJ, May 26, 2015.
o Invited Speaker, ASME-ATI-UIT 2015 – Thermal Energy Systems: Production, Storage, Utilization and the Environment, Napoli, Italy, May 18, 2015.
o Invited Speaker, 2015 Energy Forum – Nanotechnology and Energy Materials, MIT Club of Hartford, Connecticut Clean Energy Finance and Investment Authority (Connecticut Green Bank), February 7, 2015.
o Invited Speaker, 2nd International PhD Summer School – IMAGINE, DTU Energy Conversion, Technical University of Denmark, Toruplund Hotel and Conference Center, August 25-29, 2014.

Protocol Activity Status:

Technology Transfer: Collaborations and Technology Transfer

- Dr. Deryn Chu, Dr. Kyle Grew, and Dr. Xiaoming Ren, Army Research Laboratory, Adelphi, MD: ARL has validated their own Monte Carlo-based model predictions to UConn's fiber network (FN) model as they assess the effects of composition and fiber properties on overall electrospun membrane properties (i.e., anisotropy in conductivity, uptake, etc.). ARL will use our models to enable assessment of CO2 contamination in galvanic AEM devices to include cast and electrospun membranes. Alex Ph.D. Cocco, a Ph.D. graduate working on this ARO project, is currently employed as a postdoctoral fellow at the Army Research Laboratory (Adelphi, MD) to implement the rapid analytical transport network (ATN) modeling approach to heterogeneous materials in electrochemical energy systems to include batteries and fuel cells.
- Prof. Peter N. Pintauro, Department of Chemical & Biomolecular Engineering, Vanderbilt University, Nashville, TN: Provided electrospun AEM experimental data to this project for model validation. Electrospun models developed and a Ph.D. student (J. Wrubel) as part of this ARO effort may be transitioned to Prof. Pintauro's lab.
- Dr. Arata Nakajo and Prof. Jan Van herle, École de polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland: Collaborated in the creation of the Analytical Transport Network (ATN) modeling approach for heterogeneous materials in electrochemical energy systems. EPFL will use ATN as part of their simulation tools to investigate electrolyzer and fuel cell materials.
- Prof. William E. Mustain, Department of Chemical Engineering, University of South Carolina, Columbia, SC: Provided experimental data for CO2 effects on cast AEM membranes.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Wilson Chiu
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Jacob Wrubel
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Peter Damian
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Alex Cocco
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

RPPR Final Report
as of 26-Dec-2018

Participant Type: Graduate Student (research assistant)
Participant: Timothy Myles
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Staff Scientist (doctoral level)
Participant: Aldo Peracchio
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Matthew DeGostin
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Staff Scientist (doctoral level)
Participant: Brice Cassenti
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

RPPR Final Report
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Power Sources
Publication Identifier Type: DOI Publication Identifier: http://dx.doi.org/10.1016/j.jpowsour.2017.10.
Volume: 372 Issue: First Page #: 297
Date Submitted: 12/9/18 12:00AM Date Published: 11/21/17 5:00AM
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Article Title: Analytical Transport Network Theory to Guide the Design of 3-D Microstructural Networks in Energy Materials: Part 1. Flow without Reactions
Authors: Alex P. Cocco, Arata Nakajo, Wilson K. S. Chiu
Keywords: Transport, Network Theory, Rapid, Graph Theory
Abstract: We present a fully analytical, non-dimensional model – the "Analytical Transport Network Model" – for steady-state, diffusive, potential flow through a 3-D network. Employing a combination of graph theory, linear algebra, and geometry, the model explicitly relates a microstructural network's topology and the morphology of its channels to an effective material transport coefficient (a general term meant to encompass, e.g., conductivity or diffusion coefficient). The model's transport coefficient estimates exhibit good agreement with those from electrochemical fin (ECF) theory and finite element analysis (FEA), but are computed 0.5-1.5 and 5-6 orders of magnitude faster, respectively. In addition, the theory explicitly relates a number of morphological and topological parameters directly to the transport coefficient, whereby the distributions that characterize the structure are readily available for further analysis. The ATN model's speed and relative ease-of-use offer the potential to a
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

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Publication Identifier Type: Other Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 12/9/18 12:00AM Date Published:
Publication Location:
Article Title: Effects of Carbon Dioxide on the Conductivity of Electrospun and Radiation-Grafted Anion Exchange Membranes
Authors: Jacob A. Wrubel, Aldo A. Peracchio, Brice N. Cassenti, Travis J. Omasta, William E. Mustain, Kyle N. G
Keywords: Carbon Dioxide, Electrospun, Radiation-Grafted, Anion Exchange Membranes
Abstract: Electrospinning is a technology that can be used to manufacture anion exchange membranes (AEMs) with good mechanical stability while also maintaining high conductivities. The unique morphology of electrospun AEMs may affect the membrane's response to carbon dioxide absorption, a process known to degrade the conductivity of conventional AEMs. This theoretical study combines separate models describing the morphology of electrospun AEMs and the effect of CO_2 on AEMs under operating conditions. The results herein investigate the membrane's conductivity loss/reclamation as a function of key operating conditions and material properties.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
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Date Submitted: 12/9/18 12:00AM Date Published: 11/22/17 5:00AM
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Article Title: Analytical transport network theory to guide the design of 3-D microstructural networks in energy materials: Part 2. Flow with reactions
Authors: Alex P. Cocco, Wilson K.S. Chiu
Keywords: Transport, Network Theory, Rapid, Graph Theory, Reaction
Abstract: We extend the fully analytical, heuristic “Analytical Transport Network Model” for steady-state, diffusive flow in a 3-D network to account for surface reactions. In the limit of negligible reactions, the model reduces to the conserved flow solution. The extension does not increase the time required to run the model, which in Part 1 was shown to be 0.5–1.5 and 5–6 orders of magnitude faster than electrochemical fin (ECF) theory and finite element analysis (FEA) for conserved flow, respectively. The model is compared to reacting-flow ECF and FEA as well as to experiments and is demonstrated as a potentially useful heuristic for understanding the influence of morphology and topology on reactive-diffusive flow through a 3-D microstructural network.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: N **Publication Status:** 0-Other
Journal: Journal of the Electrochemical Society
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Volume: Issue: First Page #:
Date Submitted: 12/9/18 12:00AM Date Published:
Publication Location:
Article Title: Anion Exchange Membrane Fuel Cell Performance in the presence of Carbon Dioxide: An Investigation into the Self-Purging Mechanism
Authors: Jacob A. Wrubel, Aldo A. Peracchio, Brice N. Cassenti, Kyle N. Grew, Wilson K. S. Chiu
Keywords: Self-Purging Mechanism, Anion Exchange Membrane, Fuel Cell, Carbon Dioxide
Abstract: In this work we present a transient, spatially-varying AEM model to account for the carbonation process under operating conditions. Within this model we can individually simulate the chemical and electrochemical self-purging pathways, and compare the results to those observed experimentally. There are three characteristic features of the self-purging mechanism that will be investigated: (1) AEM conductivity increases as current density is increased; (2) CO2 is released into the anode gas channel corresponding to a transient current step experiment; and (3) The anode overpotential increases with increasing CO2 content, while the cathode overpotential is relatively unchanged. The goal of this work is for the self-purging model to be able to demonstrate these three phenomena. Following the determination of an appropriate self-purging model, we present a parametric investigation into this effect, and make suggestions on how to improve AEM fuel cell performance.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

CONFERENCE PAPERS:

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: 232nd ECS Meeting
Date Received: 11-Sep-2017 Conference Date: 01-Oct-2017 Date Published: 01-Oct-2017
Conference Location: National Harbor, MD
Paper Title: Anion Exchange Membrane Ionic Conductivity in the Presence of Carbon Dioxide under Fuel Cell Operating Conditions
Authors: Jacob A. Wrubel, Aldo J. Peracchio, Brice N. Cassenti, Timothy D. Myles, Kyle N. Grew, Wilson K.S. Ch
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: 232nd ECS Meeting
Date Received: 11-Sep-2017 Conference Date: 01-Oct-2017 Date Published: 01-Oct-2017
Conference Location: National Harbor, MD
Paper Title: Analytical Models for Diffusive-Reactive Flow in 3-D Microstructural Networks to Guide the Design of Electrochemical Materials
Authors: Alex P. Cocco, Arata Nakajo, Kyle N. Grew, Wilson K. S. Chiu
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: 233rd Electrochemical Society Meeting
Date Received: 09-Dec-2018 Conference Date: 13-May-2018 Date Published:
Conference Location: Seattle, WA
Paper Title: Prediciting Electrospun Anion Exchange Membrane Fuel Cell Performance Exposed to Carbon Dioxide
Authors: Jacob A. Wrubel, Aldo J. Peracchio, Brice N. Cassenti, Kyle N. Grew, Wilson K. S. Chiu
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: 233rd Electrochemical Society Meeting
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Paper Title: The Analytical Transport Network Model for Diffusive-Reactive Flow in 3-D Microstructural Networks: A Computationally Economical Model for Potential Use in Multi-Scale Modeling Efforts
Authors: A. P. Cocco, A. Nakajo, K. N. Grew, W. K. S. Chiu
Acknowledged Federal Support: **Y**

DISSERTATIONS:

Publication Type: Thesis or Dissertation
Institution: University of Connecticut
Date Received: 11-Sep-2017 Completion Date: 11/26/16 9:02PM
Title: Three-Dimensional Imaging Methods and Analytical Transport Network Theory to Guide the Characterization and Design of Energy Materials
Authors: Alex P. Cocco
Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation
Institution: University of Connecticut
Date Received: 09-Dec-2018 Completion Date: 7/31/14 10:04PM
Title: Applicability of Effective Medium and Transport Theories to Fuel Cell Materials
Authors: Timothy Myles
Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation
Institution: University of Connecticut
Date Received: 09-Dec-2018 Completion Date: 8/3/15 4:00AM
Title: Microstructural Design Models for Electrochemical Electrodes
Authors: Matthew DeGostin
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 26-Dec-2018

Final Technical Report

ARO Grant # 63055-CH
(Reporting Period: June 23, 2014 – August 31, 2018)

Carbonate and Hydroxide Ion Transport in Alkaline Anion Exchange Materials

Wilson K. S. Chiu
Department of Mechanical Engineering
University of Connecticut
Storrs, CT 06269-3139
wchiu@engr.uconn.edu

Table of Content **Page**

Objective
Even though there is significantly greater understanding of the proton transport mechanism in the cation exchange membranes, the dominant carbonate and OH^- ion transport mechanisms in the anion exchange membrane (AEM) are yet unclear. Preliminary results have shown that we can successfully predict OH^- conductivity, ion dissociation processes, and water flux in the AEM This project will obtain fundamental understanding into the formation and transport of carbonate ions and hydroxide ions in AEM material, and then to examine solutions for AEM stability and performance in the presence of carbon dioxide.

Approach
A detailed understanding of how carbonate ions and hydroxide ions form and transport in AEM material is needed in order to understand how they affect the ionic conductivity and stability of the AEM material. This will be achieved by creating analytical/numerical models to accurately describe the formation and transport of carbonate ions and hydroxide ions in the AEM, validating the model using experimental data obtained provided by our collaborators at the Army Research Laboratory (Dr. Deryn Chu, Dr. Kyle Grew, and Dr. Xiaoming Ren), Vanderbilt University (Prof. Peter Pintauro), and from the published literature, and exploring solutions for AEM stability and performance in the presence of carbon dioxide.

Relevance to the Army
There are considerable Army power and energy needs including Soldier & Sensor power, Field/Base power, Vehicle power and Air Platform power. The Army has targeted fuel cells as a candidate for portable power, APUs, UAV/UGV, and unattended ground sensors. Applications include methanol-fueled fuel cells for Future Warriors (72 hour mission), and logistic-fueled fuel cells for 96 hour missions. There is significant interest in alkaline fuel cells utilizing solid-polymer alkaline anion exchange membranes (AEM), which are the high pH equivalent to proton exchange membranes (e.g. Nafion). The alkaline membrane fuel cell (AMFC) provide opportunities for the direct use of alcohol fuels. As detailed in the Army Research Office *2011 Alkaline Membrane Fuel Cell Workshop Final Report*, the AMFC is seen as a promising candidate for high energy density portable power applications, and specifically those in the vicinity of 20-100 W with some unique opportunities for small passive devices in the 1-5 W range.

Accomplishments
This project has achieved several major accomplishments:
- Used analytical Effective Media Theory to successfully estimate the electrospun AEM's hydroxide conductivity.
- Performed a collaborative study with ARL to investigate the effect of CO_2 on Nafion material.
- Obtained fundamental understanding into the transient formation and transport of carbonate ions and hydroxide ions in AEM material in the presence of CO_2.
- Created Fiber Network (FN) ion transport model to simulate the three-dimensional fibrous microstructural morphology and predict properties that result from the electrospinning membrane fabrication process.
- Examined the effect of CO_2 on cast and electrospun AEM.
- Identified potential CO_2 mitigation strategies, e.g. self-purging, electrospinning.
- Created a fully analytical Analytical Transport Network Model to explicitly relate a microstructural network's topology and the morphology of its channels to an effective

material transport coefficient with computational time that is 5–6 orders of magnitude faster than finite element analysis.

Collaborations and Technology Transfer

- Dr. Deryn Chu, Dr. Kyle Grew, and Dr. Xiaoming Ren, Army Research Laboratory, Adelphi, MD: ARL has validated their own Monte Carlo-based model predictions to UConn's fiber network (FN) model as they assess the effects of composition and fiber properties on overall electrospun membrane properties (i.e., anisotropy in conductivity, uptake, etc.). ARL will use our models to enable assessment of CO_2 contamination in galvanic AEM devices to include cast and electrospun membranes. Alex Ph.D. Cocco, a Ph.D. graduate working on this ARO project, is currently employed as a postdoctoral fellow at the Army Research Laboratory (Adelphi, MD) to implement the rapid analytical transport network (ATN) modeling approach to heterogeneous materials in electrochemical energy systems to include batteries and fuel cells.
- Prof. Peter N. Pintauro, Department of Chemical & Biomolecular Engineering, Vanderbilt University, Nashville, TN: Provided electrospun AEM experimental data to this project for model validation. Electrospun models developed and a Ph.D. student (J. Wrubel) as part of this ARO effort may be transitioned to Prof. Pintauro's lab.
- Dr. Arata Nakajo and Prof. Jan Van herle, École de polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland: Collaborated in the creation of the Analytical Transport Network (ATN) modeling approach for heterogeneous materials in electrochemical energy systems. EPFL will use ATN as part of their simulation tools to investigate electrolyzer and fuel cell materials.
- Prof. William E. Mustain, Department of Chemical Engineering, University of South Carolina, Columbia, SC: Provided experimental data for CO_2 effects on cast AEM membranes.

Resulting Journal Publications

1. Papers Published in Peer-Reviewed Journals (8)

1. A. P. Cocco, A. Nakajo, and W. K. S. Chiu, "Analytical Transport Network Theory to Guide the Design of 3-D Microstructural Networks in Energy Materials: Part 1. Flow without Reactions," *J. Power Sources*, 372: 297-311, 2018.
2. A. P. Cocco and W. K. S. Chiu, "Analytical Transport Network Theory to Guide the Design of 3-D Microstructural Networks in Energy Materials: Part 2. Flow with Reactions," *J. Power Sources*, 372: 312-324, 2018.
3. J. A. Wrubel, A. A. Peracchio, B. N. Cassenti, T. D. Myles, K. N. Grew, and W. K. S. Chiu, "Anion Exchange Membrane Ionic Conductivity in the Presence of Carbon Dioxide under Fuel Cell Operating Conditions," *J. Electrochem. Soc.*, 164(12): F1-F11, 2017.
4. M. B. DeGostin, A. A. Peracchio, T. D. Myles, B. N. Cassenti, and W. K. S. Chiu, "Charge Transport in the Electrospun Nanofiber Composite Membrane's Three-Dimensional Fibrous Structure," *J. Power Sources,* 307: 538-551, 2016.
5. X. Ren, T. D. Myles, K. N. Grew, and W. K. S. Chiu, "Carbon Dioxide Transport in Nafion 1100 EW Membrane and in a Direct Methanol Fuel Cell," *J. Electrochem. Soc.,* 162: F1221-F1230, 2015.

6. T. D. Myles, K. N. Grew, A. A. Peracchio, and W. K. S. Chiu, "Transient Ion Exchange of Anion Exchange Membranes Exposed to Carbon Dioxide," *J. Power Sources*, 296: 225-236, 2015.
7. T. D. Myles, A. A. Peracchio, and W. K. S. Chiu, "Extension of Anisotropic Effective Medium Theory to Account for an Arbitrary Number of Inclusion Types," *J. Appl. Phys.,* 117: 025101, 2015.
8. T. D. Myles, A. A. Peracchio, U. Pasaogullari, and W. K. S. Chiu, "Application of a New Effective Medium Formulation to Account for Transport due to Fiber and Web-like Inclusions in Gas Diffusion Layers," *J. Electrochem. Soc.*, 162: F645-F650, 2015.

2. Manuscripts to be Submitted (2)

1. J. A. Wrubel, A. J. Peracchio, B. N Cassenti, K. N. Grew, and W. K. S. Chiu, "Anion Exchange Membrane Fuel Cell Performance in the presence of Carbon Dioxide: An Investigation into the Self-Purging Mechanism," to be submitted, 2018.
2. J. A. Wrubel, A. A. Peracchio, B. N. Cassenti, T. J. Omasta, W. E. Mustain, K. N. Grew and W. K. S. Chiu, "Effects of Carbon Dioxide on the Conductivity of Electrospun and Radiation-Grafted Anion Exchange Membranes," to be submitted, 2018.

3. Conference Proceedings, Presentations and Abstracts (4)

1. J. A. Wrubel, A. J. Peracchio, B. N. Cassenti, K. N. Grew and W. K. S. Chiu, "Predicting Electrospun Anion Exchange Membrane Conductivity in the Presence of Carbon Dioxide," *233rd Electrochemical Society Meeting*, Abstract No. 108354, Seattle, WA, May 13-27, 2018.
2. A. P. Cocco, A. Nakajo, K. N. Grew and W. K. S. Chiu, "The Analytical Transport Network Model for Diffusive-Reactive Flow in 3-D Microstructural Networks: A Computationally Economical Model for Potential Use in Multi-Scale Modeling Efforts," *233rd Electrochemical Society Meeting*, Abstract No. 108886, Seattle, WA, May 13-27, 2018.
3. J. A. Wrubel, A. J. Peracchio, B. N. Cassenti, T. D. Myles, K. N. Grew and W. K. S. Chiu, "Anion Exchange Membrane Ionic Conductivity in the Presence of Carbon Dioxide under Fuel Cell Operating Conditions," *232nd Electrochemical Society Meeting*, Abstract No. 105132, National Harbor, MD, October 1-6, 2017 (*ECS Trans.*, 80, 2017).
4. A. P. Cocco, A. Nakajo, K. N. Grew and W. K. S. Chiu, "Analytical Models for Diffusive-Reactive Flow in 3-D Microstructural Networks to Guide the Design of Electrochemical Materials," *232nd Electrochemical Society Meeting*, Abstract No. 104760, National Harbor, MD, October 1-6, 2017.

Personnel Involved in this Project

- Jacob A. Wrubel, Ph.D. candidate, expected May, 2019
- Peter J. Damian, M.S., December, 2018
- Alex P. Cocco, Ph.D., December, 2016
- Matthew B. DeGostin, M.S., August 2015
- Timothy D. Myles, Ph.D., December, 2014
- Aldo P. Peracchio, Staff Scientist
- Brice Cassenti, Staff Scientist

Awards, Honors and Appointments

- Alex P. Cocco, postdoctoral fellow, Army Research Laboratory, Adelphi, MD.
- Wilson K. S. Chiu

Editorial Activities

- Editor, *ASME Journal of Electrochemical Energy Conversion and Storage*, 2016-2020.
- Editorial Board, *Scientific Reports*, Nature Publishing Group, since 2015.

Advisory Boards / Review Committees

- NSLS-II Microscopy and Imaging Proposal Review Panel, *National Synchrotron Light Source II, Brookhaven National Laboratory, NY*, 2017 – 2020.
- NSLS-II Science Advisory Committee (SAC) Review Committee, HXN Triennial Beamline Review, *National Synchrotron Light Source II, Brookhaven National Laboratory, NY*, 2018.
- Full field X-ray Imaging (FXI) Beamline Advisory Team, *National Synchrotron Light Source II, Brookhaven National Laboratory, NY*, 2012 – 2017 (Chair, 2017).
- Imaging Beam Line Review Committee, *Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory*, Stanford, CA, 2015.

Keynote/Invited Speaker:

- Invited Speaker, Army Research Laboratory, Adelphi, MD, September 18, 2018.
- Invited Speaker, Focused Session on *Materials Issues in Nuclear Waste Treatment and Disposal*, *8th Forum on New Materials, 14th International Conference on Modern Materials and Technologies (CIMTEC 2018)*, Perugia, Italy, June 10-14, 2018.
- Invited Department Seminar Speaker, *University of California, Irvine*, *Department of Mechanical and Aerospace Engineering*, Irvine, CA, June 1, 2018.
- Invited Department Seminar Speaker, *Technical University of Denmark, Department of Energy Conversion and Storage*, Riso, Denmark, November 14, 2017.
- Invited Department Seminar Speaker, *Clemson University, Department of Materials Science and Engineering,* Clemson, SC, September 14, 2017.
- Invited Speaker, *OFS Specialty Photonics Division*, Avon, CT, July 14, 2017.
- Keynote Speaker, *7th International Symposium on Advances in Computational Heat Transfer (CHT-17)*, Naples, Italy, May 28-June 1, 2017.
- Invited Speaker, *IEK-1 Materials Synthesis and Processing, Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH,* Jülich, Germany, September 22, 2016.
- Invited Speaker, *Indo-US Science and Technology Forum on Recent Advances in Multiscale, Multiphysics Analysis of Energy Conversion in Li-Ion Batteries*, Mumbai, India, June 17-19, 2016.
- Invited Speaker, *12th International Conference on Durability of Composite Systems (DURACOSYS)*, Arlington, TX, June 12-15, 2016.
- Invited Speaker, *Photon Science Seminar Series*, SLAC National Accelerator Laboratory, Stanford, CA, May 25, 2016.
- Invited Department Seminar Speaker, *EPFL Valais-Wallis,* Sion, Switzerland, March 24, 2016.
- Keynote Speaker, *13th Symposium on Modeling & Experimental Validation of Fuel Cells, Batteries & Electrolysers (MODVAL13)*, Lausanne, Switzerland, March 22-23, 2016.
- Invited Speaker, *TMS 2016 145th Annual Meeting & Exhibition*, Nashville, TN, February 15, 2016.

- Keynote Speaker, *International Conference on Computational & Experimental Engineering and Sciences (ICCES'15),* Reno, NV, July 23, 2015.
- Invited Speaker, *Duracell Technical Center*, Berkshire Corporate Park, Bethel, CT, Monday, June 8, 2015.
- Invited Speaker, *6th International Symposium on Computational Heat Transfer (CHT-15)*, Rutgers University, Piscataway, NJ, May 26, 2015.
- Invited Speaker, *ASME-ATI-UIT 2015 – Thermal Energy Systems: Production, Storage, Utilization and the Environment*, Napoli, Italy, May 18, 2015.
- Invited Speaker, *2015 Energy Forum – Nanotechnology and Energy Materials, MIT Club of Hartford*, Connecticut Clean Energy Finance and Investment Authority (Connecticut Green Bank), February 7, 2015.
- Invited Speaker, *2nd International PhD Summer School – IMAGINE, DTU Energy Conversion, Technical University of Denmark*, Toruplund Hotel and Conference Center, August 25-29, 2014.

Description of Technical Achievements

1. Effective Media Theory

Models for predicting the effective conductivity of complex combinations of materials made up of conducting and insulating components have been created using Effective Medium Theory (EMT). EMT typically relies on idealizing the morphology of a mixture such that analytical solutions of the electric field are possible (e.g., Laplace's Equation), then combines these solutions to obtain an estimate of the effective conductivity of the mixture. Under this program, classical EMT methods, (specifically Bruggeman's unsymmetric theory), have been extended to include multiple inclusion types and also to apply these extensions to transport through materials including fiber and web-like inclusions. This effort has resulted in two journal articles published in the *Journal of Applied Physics* [1], and the *Journal of the Electrochemical Society* [2].

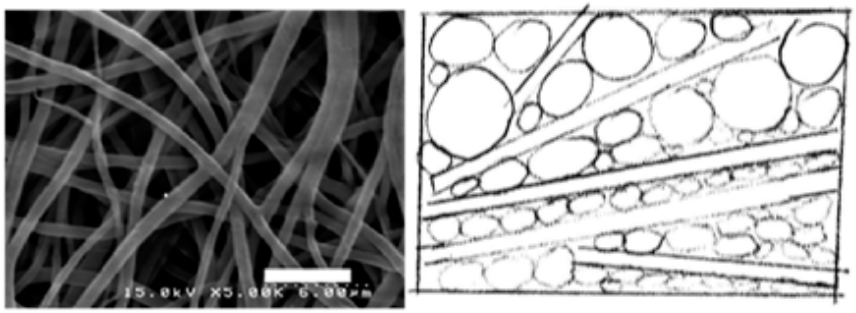


Figure 1. (left) SEM micrograph showing the electrospun AEM's nanofiber morphology (from [3]), and (right) Effective Media Theory approximation of the nanofiber structure.

This EMT model was used to obtain an approximate early estimate of the fiber network conductivity while the more applicable fiber network model is being developed. The morphology of the fiber network shown in Fig. 1 (left) was coarsely approximated by a collection of rods and spheres, with the rods representing the conductors and the spheres the insulating material, (see Fig. 1 right). In-plane effective conductivities for two cases were chosen from data provided by our collaborator, Prof. Peter Pintauro (see [3], Fig. 6, for 7% Crosslinking Degree): volume fractions of the conducting material were 0.68 and 0.59 with corresponding effective conductivities of 65 and 58 mS/cm, respectively. Taking the spheres as perfect insulators, the resulting fiber conductivities were estimated using EMT to be 119 and 133 mS/cm. Considering the level of approximation made to fit the model to the fiber network morphology, the results seemed reasonably close. Other similar approximations using the EMT were made utilizing rods (conductors) and spheroids (insulators) with similar results. The next step will be to compare to experimental data for fiber conductivity provided by Prof. Pintauro, and consider a more detailed description of the nanofiber morphology using the Fiber Network Theory.

2. Effect of Carbon Dioxide on Nafion Material

In Nafion, CO_2 can be involved in the mass transport and the balance of materials in the electrode reactions for those fuel cells fed with hydrocarbon fuels, either directly such as in direct methanol fuel cells (DMFC) or through fuel reformation. In this collaboration with ARL, we investigated CO_2 transport in Nafion membranes (E.W. 1100) under various hydration and

temperature conditions using an IR based CO_2 detector to monitor both the transient and steady state CO_2 permeate flux through the membranes.

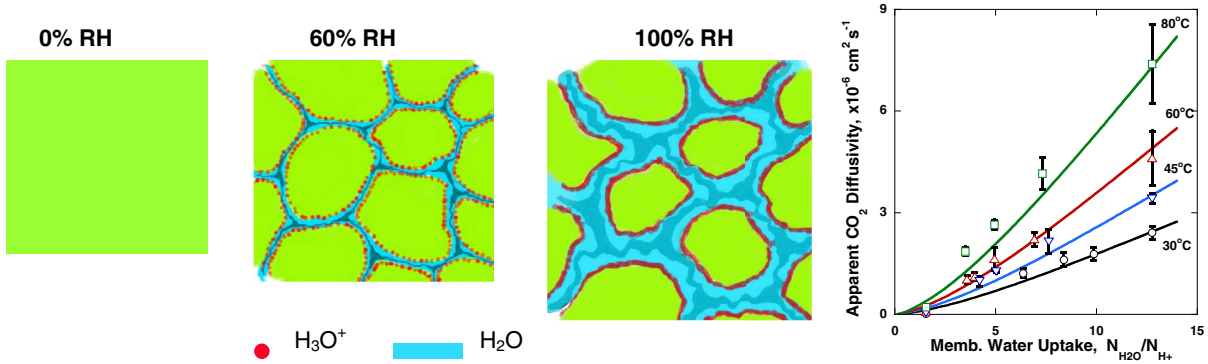


Figure 2. Conceptual illustration showing changes in the Nafion nanostructure during water uptake. Water channels can straighten and grow in dimensions and interconnect with increased membrane hydration level (% RH), providing facile pathways for CO_2 transport. The apparent CO_2 diffusivity was measured (symbols) and compared to theory (curves) in Nafion membranes at various water content and temperature. Figure is from [4].

It was found that CO_2 diffusivity in a dry membrane is very low, but it increases rapidly with the membrane-hydration level as shown in Fig. 2. A high CO_2 solubility was observed in dry membranes as compared to those in humidified membranes, for which the CO_2 solubility remains nearly invariant to the membrane hydration level at a given temperature. By comparing the measured data with those calculated for the CO_2 transport solely in the water channels, it is concluded that the CO_2 transport in Nafion membranes is dominated by its transport in the water channels shown in Fig. 2. Carbon dioxide and methanol crossover in a DMFC configuration were also examined. By operating the DMFC configuration in methanol electrolysis mode, the CO_2 crossover rate was measured, which can be used to correct the methanol crossover measurements from measuring CO_2 flux in the DMFC cathode effluent stream, and to derive the local CO_2 partial pressure at the DMFC anode catalyst layer. This effort has resulted in a journal article published in the *Journal of the Electrochemical Society* [4].

3. Transient Formation and Transport of Carbonate and Hydroxide Ions in AEM

The transient ion exchange of AEM material exposed to CO_2 was investigated. Figure 3 shows the contribution of the individual anions to the overall IEC are shown for the Tokuyama A201 and the ETFE radiation-grafted membranes exposed to atmospheric air (385 ppm) at room temperature at the fully hydrated condition. In these studies, the membrane material is not in an active fuel cell.

The solid lines represent the total ion concentrations while the dotted lines represent the dissociated ion concentrations. The A201 and the ETFE membranes display the same general trend where the concentration of the hydroxide species drops off sharply once the carbon dioxide is introduced. Initially, the hydroxide is replaced solely by carbonate, until the hydroxide has been completely depleted. This can be referred to as the *hydroxide depletion region*. Once the hydroxide has been completely depleted, some of the carbonate is converted to bicarbonate until equilibrium is reached. This second characteristic portion of the transient behavior can be referred to as the *bicarbonate accumulation region*. A discrepancy of the conversion time between the two membrane types is observed with the A201 membrane taking upwards of 30

minutes to convert the hydroxide while the ETFE takes about 60 minutes. Since the ETFE membrane thickness at 80 μm is much thicker than the 28 μm A201 membrane, the conversion time for the ETFE membrane should be much longer due to diffusion through the material thickness. However, if we normalize the diffusion time based on diffusion length, the diffusion times should match the case of a pure diffusion. Interestingly, there is still a significant difference in the normalized diffusion times, suggesting the importance of kinetics in the carbon dioxide accumulation.

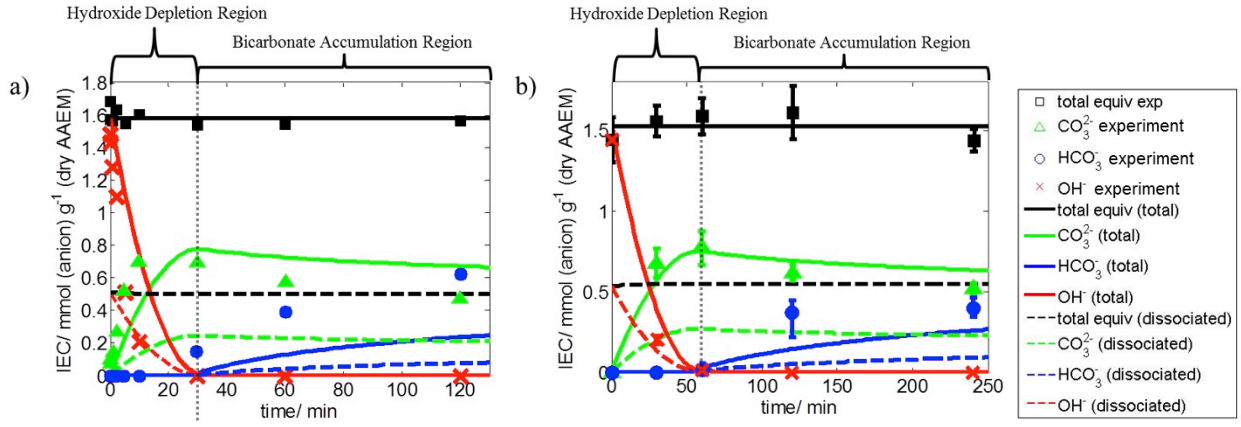


Figure 3. Comparison between titration data available in the literature with predictions: (a) A201 data from Yanagi and Fukuta [5] and (b) ETFE data from Kizewski et al. [6]. The dotted vertical line running through both figures separates what is referred to as the hydroxide depletion region and the bicarbonate accumulation region. Figure is from [7].

In this study, the transient ionic conductivity and transient volumetric absorption of carbon species for two AEM materials, namely Tokuyama A201 [8] and ETFE [9], are shown in Fig. 4. The transient behavior of the conductivity can be explained by the considering the relative contributions to ionic conductivity of each of the anionic species in the membrane (the dissociated hydroxide, bicarbonate, and carbonate). The ionic conductivities of each of these species can be ranked since it is clear that hydroxide has the highest conductivity due to the high value of the diffusivity and the low value of the molecular mass. Between the bicarbonate and the carbonate, the diffusivities and molecular masses are similar, but the valance of -2 for the carbonate gives it a higher conductivity. With this insight, the transient ionic conductivity behavior in Fig. 4 can be rationalized where the initial sharp decrease is due to the rapid loss of hydroxide in the membrane. Steady state values for various ionic forms are used for validation exercise to the proposed steady state form of the membrane. In the case of the Tokuyama membrane, this comparison was made by Grew et al. [8] and is shown in Fig. 4a. For the ETFE membrane there is, to the author's knowledge, no air equilibrated data available, but there are measurements available for the hydroxide form ETFE membrane at the relevant conditions shown in Fig. 4b made by Varcoe et al. [9]. As can be seen in Fig. 4, the comparisons are favorable giving further credibility to the results. This effort has resulted in a journal article published in the *Journal of Power Sources* [7].

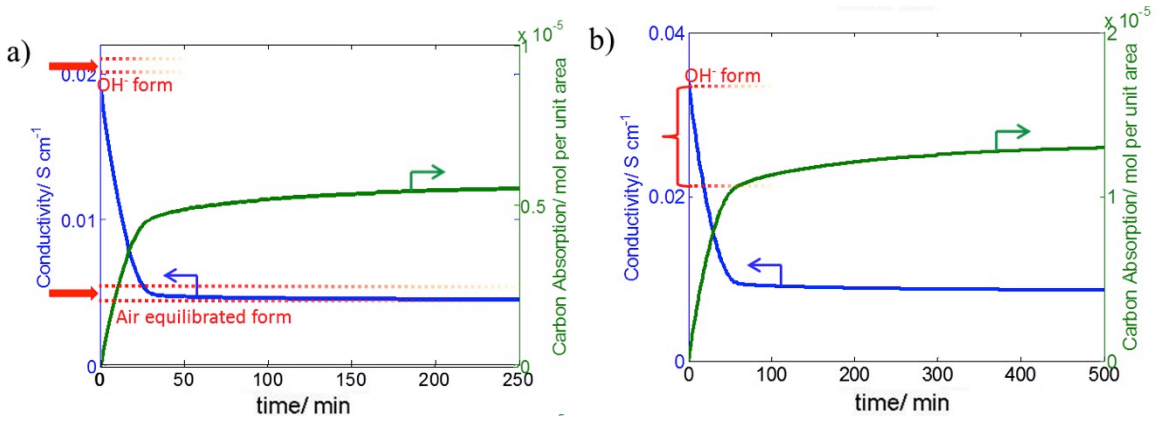


Figure 4. Transient ionic conductivity (left axis) and transient volumetric absorption of carbon species (right axis) for (a) Tokuyama A201 membrane and (b) ETFE membrane. The red dotted lines represent the range of experimental data taken from the literature for equilibrium conditions (data from Grew et al. [8] for the A201, data from Varcoe et al. [9] for the ETFE). Figure is from [7].

4. Fiber Network (FN) Ion Transport Model for Electrospun AEM Microstructure

Polymer electrolyte membrane material fabricated by electrospinning have unique morphologies based on the presence of highly inter-connected three-dimensional networks of nanofibers. Recently, proton exchange membrane (PEM) and anion exchange membrane (AEM) materials have been fabricated where a charge conducting fiber network is completely surrounded by an inert, hydrophobic, insulating matrix phase [10], [11]. These materials have exhibited high ionic conductivities as well as good mechanical stability and controlled swelling due to the presence of the supporting matrix. Even though transport theory has been developed to describe ion transport in ion exchange membranes (e.g., [12], [13]), it is unclear how the nanofiber morphology in electrospun membrane may affect ion transport within the membrane material. In the interest of studying charge transport in these electrospun membranes, a number of transport models, both existing and newly developed, have been utilized to predict membrane performance (swelling, conductivity) taking into account their fibrous network morphologies.

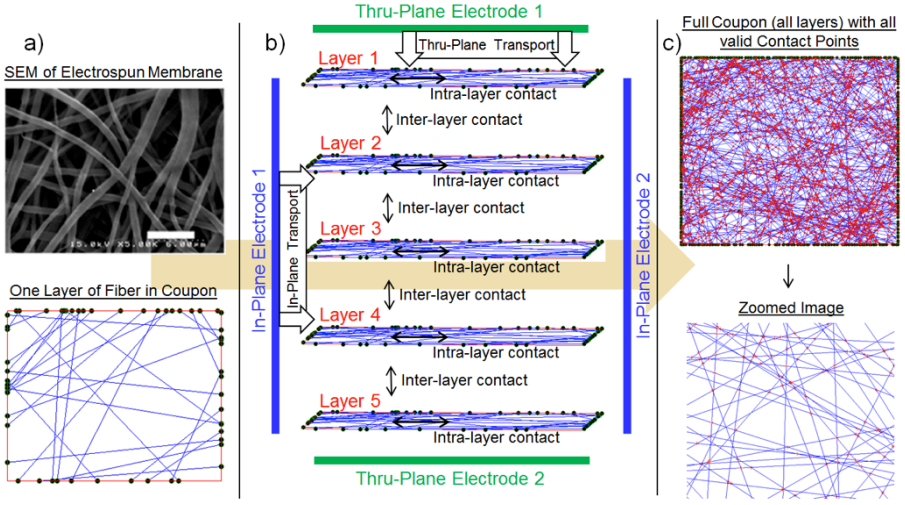


Figure 5. In the Fiber Network model, a single layer of fibers is randomly generated (a), and is stacked with other layers (b) to produce a full coupon (c) which is statistically representative of an electrospun membrane. In-plane and thru-plane conduction cases are pictured in (b). Figure is from [14].

The Fiber Network (FN) model is one such model used to study charge transport, where electrospun membranes are modeled as random resistor networks, which are then solved by Kirchhoff's circuit laws to obtain in-plane and thru-plane membrane conductivities. This model first assumes that a full membrane (order of 1 cm by 1 cm) shown in Fig. 5 can be approximated by a representative coupon of much smaller size (roughly 20 mm by 20 mm), with transport properties that are statistically representative of the membrane. The coupon's size is initially defined and then fibers (represented by straight, randomly oriented line segments) are randomly deposited until the coupon reaches a certain volume fraction of conducting fiber. This process includes fiber layering, which is used to approximate ionic contact between conducting fibers and any 3-D transport that may occur, which is relevant for both in-plane and thru-plane conduction. Contact points between fibers are found, and then resistor networks are constructed, where each segment of fiber is represented by a charge conducting, cylindrical electrochemical fin ([15], [16]). he membranes are allowed to swell with water, whereupon coupon dimensions and fiber dimensions are modified accordingly based on two swelling models. One assumes isotropic swelling of the coupon, the other assumes the coupon only swells in the thickness direction (and the fiber only swells radially). In the formation of a coupon, beginning from an SEM of an electrospun AEM is shown in Fig. 5, single layers of fibers are generated and stacked on top of one another, whereupon a full coupon is constructed allowing in-plane and thru-plane conduction to be modeled.

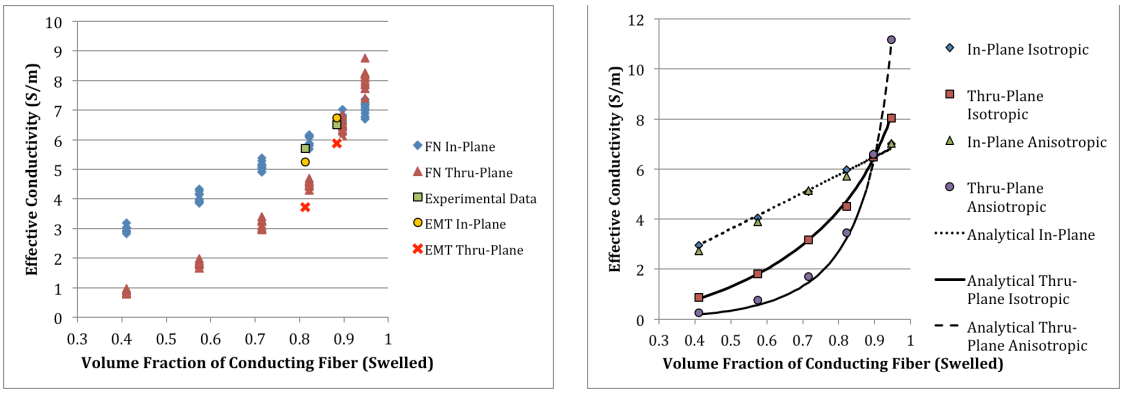


Figure 6. (left) Fiber network (FN) model predictions for in-plane and thru-plane ionic conductivity of electrospun AEMs versus swelled volume fraction, and experimental measurements of in-plane conductivity. Predictions were compared to Effective Media Theory (EMT) from this project [1], [2], and experimental results from Park et al. [3]. (right) A comparison of the in-plane and thru-plane conductivity trend for electrospun AEM material undergoing isotropic and anisotropic swelling due to fiber orientation. Figure is from [14].

The hydroxide conductivity of electrospun AEM material predicted by FN theory is shown in Fig. 6 (left). The AEM material is composed of chloromethylated polysulfone (CMPSF) conducting fibers with inert reinforcing poly(phenylsulfone) PPSU fibers to form a nanofiber composite mat. Both fiber types exhibited an average fiber diameter, before swelling, of roughly 700 nm. Fiber network predictions were compared to Effective Media Theory (EMT) developed during the first year of this project ([1], [2]), and to experimental results from Prof. Pintauro at Vanderbilt University [3]. The fiber conductivity calculated from the FN model compares reasonably well to the EMT predictions. Unlike FN theory, EMT being an effective theory cannot predict a specific 3-D morphology for a given property. Validation to experimental measurements indicate that FN model predictions fall within the range that occurs due to randomness in the coupon morphology. It is interesting to note that in-plane conductivity yields

linear behavior, which is consistent with the analytical in-plane conductivity model presented in this work. Thru-plane conductivity, however, appears to vary non-linearly with volume fraction. A general trend is observed that low volume fractions yield thru-plane conductivity that is lower than in-plane conductivity.

This variation in functional trend between in-plane and thru-plane conductivity is further illustrated in Fig. 6 (right), and can be explained by considering how the inter-connectivity of the fiber network structure change with volume fraction. In the case of in-plane conductivity, beginning with a fiber that spans the width of the membrane between electrodes, adding additional fibers (thus increasing the volume fraction) will not decrease the distance ions must travel between electrodes. Instead, additional fibers merely act as additional resistors that are roughly in parallel with one another, and of approximately the same length; resulting in ionic conductivity that varies linearly with volume fraction. Regarding thru-plane conduction, when relatively few fibers exist through the thickness of the membrane, few thru-plane transport paths exist because of a weak presence of intra- and inter-layer contact points. Thus, in a discrete network, ions must travel a significant distance within each layer (in-plane) in addition to between layers to span the thickness. High volume fractions of conducting fiber result in additional contact points and thus additional thru-plane transport pathways, resulting in a non-linear increase in contact points with the number of fibers in a layer.

AEM material is swelled with water to facilitate the transport of ions. In this study, we investigate two forms of swelling. Anisotropic swelling occurs when the fiber swelling in the radial direction is dominant and volumetric swelling is manifested mainly as an increase in the coupon thickness. Isotropic swelling will increase all coupon dimensions. Both forms of swelling exhibit different behavior on ionic conductivity, as shown in Fig. 6. As volume fraction is increased, fiber length does not increase during anisotropic swelling; therefore much higher effective thru-plane conductivities at high volume fractions result since only the diameter of conducting fibers is increasing. In contrast, the increase in fiber length and slightly lower increase in fiber diameter during isotropic swelling yields a more moderate increase in effective conductivity at high volume fractions. For low volume fractions, the low connectivity of the structures is assumed to dominate, where an increase in coupon thickness that result from anisotropic swelling are hypothesized to result in lower conductivities than the corresponding isotropic swelling case. In summary, an accurate model was successfully created to predict the properties of electrospun AEM material. This FN model will be used to further understand the formation and transport of carbonate ions and hydroxide ions in electrospun AEM material. This effort has resulted in a journal article published in the *Journal of Power Sources* [14].

5. Effect of CO_2 on Cast AEM under Fuel Cell Conditions

The ionic conductivity of cast and electrospun AEM in the presence of carbon dioxide is explored under fuel cell operating conditions to obtain insight into how CO_2 affects AEM material, and applied that knowledge to explore how AEM performs in a fuel cell. A mitigation scheme is also proposed, in which operation under high current density may recover AEM ionic conductivity due to high hydroxide ion concentration displacing lower ionic conducting carbonate and bicarbonate ions.

The transient, spatially-averaged N-P equations were solved numerically [17] to yield the transient concentrations of each species in a cast AEM. The ionic concentrations were then be

used to predict the membrane's ionic conductivity using the Dusty-Fluid Model, as shown in Figs. 7a-c. The plots are normalized to the membrane conductivity for the pure OH^- state when the cathode gas stream is free of CO_2. The transient behavior of the membrane is investigated in Fig. 7a. It can be seen that as current density increases, the conductivity rate of change increases as well. In addition, the maximum recovery compared to the pure OH^- state (steady state value) is greater. Therefore, in the interest of maintaining high membrane conductivity, the cell should be operated at the highest possible current density. However, degradation aspects such as the membrane drying out are not considered, which may become important at high current densities. Fig. 7b shows that the conductivity is significantly affected by operating temperature. This is mostly due to the effects of temperature on the equilibrium constants for the bicarbonate- and carbonate-forming reactions, which are shifted to favor the reactants as temperature is increased. This increases the equilibrium value of OH^- in the membrane, which increases the conductivity.

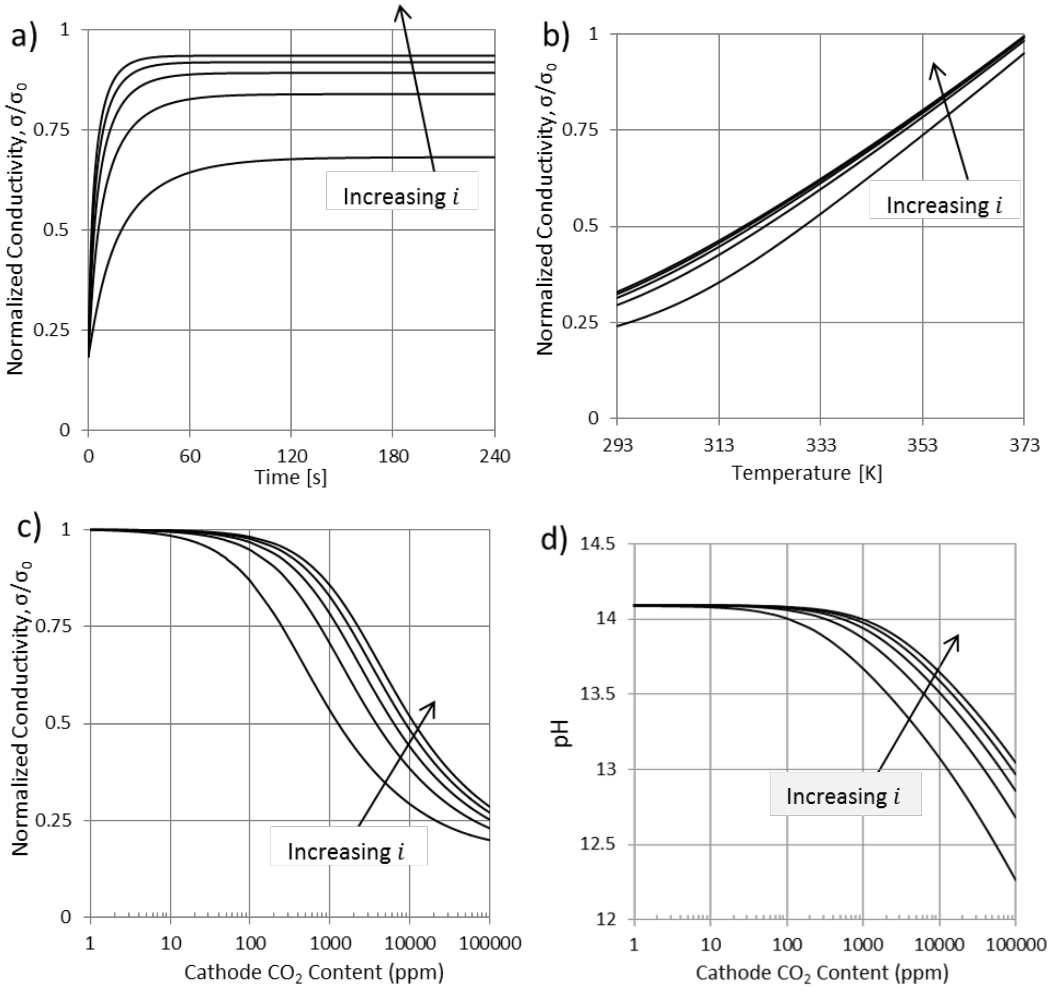


Figure 7. Conductivity vs. a) Time (membrane initially in carbonate state), b) Temperature, and c) Cathode CO_2 content (shown as ppm of total gas), and d) pH vs. Cathode CO_2 content (shown as ppm of total gas) of an A201 cast AEM membrane at different operating currents (i=100, 300, 500, 700, 900 mA/cm^2). Figures are from [17].

Figure 7c affirms the experimentally reported trend [18]–[20] that membrane conductivity decreases as the cathode CO_2 content is increased. Increasing the cathode CO_2 content (displayed as ppm of total gas in the figure) increases the free-stream CO_2 concentration in the cathode gas stream, which shifts the bicarbonate- and carbonate-forming reactions toward the products, thus

favoring carbonate (CO_3^{2-}) and bicarbonate ions (HCO_3^-) in the membrane. The onset of conductivity loss occurs between 10-100 ppm CO_2 in the cathode gas stream, depending on the current, which demonstrates the importance of maintaining CO_2-free gas streams. In the first regime, up to 10-100 ppm CO_2 depending on the operating current, the ORR is able to supply enough OH^- (especially at higher current densities) to displace the CO_3^{2-} and HCO_3^- produced by the relatively low levels of CO_2, so the conductivity drop is not as pronounced. As the incoming CO_2 concentration increases (> 10-100 ppm range), the CO_2 flux into the membrane is greater, and the concentrations of CO_3^{2-} and HCO_3^- rise accordingly, decreasing the conductivity of the membrane. Although there appears to be a third regime where the conductivity drop begins to plateau, free stream CO_2 concentrations greater than 10% were not investigated since some assumptions of the model may become invalid at high concentrations. For instance, reduction of CO_2 at the cathode may start to contribute to the total current if it is concentrated enough, which would decrease the flux of OH^- ions due to the oxygen reduction reaction (ORR). Furthermore, the accuracy of the Henry's Law absorption model decreases for more concentrated gases.

In addition to conductivity, the pH of the membrane as a function of operating current and cathode CO_2 content is shown in Fig. 7d. The pH is corrected for the ionic strength of the membrane using the Davies equation to find the hydrogen ion activity. The membrane's pH drops as the cathode CO_2 content increases since the resulting CO_3^{2-} and HCO_3^- ions displace OH^- from the membrane. In addition, there is less of a pH drop at higher current densities due to the influx of OH^- from the ORR. The results of Figs. 1c and 1d combined present an interesting optimization problem for the use of AEM fuel cells. Clearly the presence of CO_2 in the cathode gas feed results in a drop in the membrane's conductivity. However the drop in pH due to CO_2 interactions results in a less caustic environment, which leads to reduced electrolyte degradation and conductivity loss [21].

These results were recently published in the *Journal of Electrochemical Society* [17] and presented at the *232nd Electrochemical Society Meeting* (Abstract No. 105132, National Harbor, MD, October 1-6, 2017; ECS Trans., 80, 2017). An additional journal manuscript that discusses the self-purging mechanism will be submitted in the near future.

6. Effect of CO_2 on Electrospun AEM under Fuel Cell Conditions

Another opportunity to create AEMs with similar features to traditional membrane supports without adding manufacturing steps is to make electrodes by electrospinning. Electrospinning is a technology that provides an opportunity to decouple aspects of a membrane's conductivity and stability. Specifically, this approach can enable membranes with increased IEC values while also maintaining their mechanical integrity [11]. Electrospun AEMs are typically crosslinked polymer composites that consist of a hydrophilic ion-conducting phase embedded in an inert, supporting phase. The supporting phase is often hydrophobic, and is used to control swelling. This enables a relatively higher IEC for the ionomer phase while providing mechanical strength and stability. Electrospinning is a forced assembly technique that combines the dissimilar polymers into a well-dispersed mat, which can then be further processed into a fully dense membrane [11]. The conductivity of electrospun AEMs strongly depends on the volume fraction of the ionomer phase, f_f, with pristine conductivities up to 65 mS-cm^{-1} having been reported [11] for 65 wt. % ionomer fiber membranes in liquid water at 23 °C.

It is known from previous work that CO_2 can degrade membrane performance upon absorption by partaking in carbonate- and bicarbonate-forming reactions [7] (CO_3^{2-} and HCO_3^-, respectively). The formation of these less mobile ions lowers the membrane's conductivity. Because the morphology and bulk material properties of electrospun AEMs can be considerably different from cast AEMs, it is worthwhile to examine their susceptibility to CO_2. Furthermore, the tunability of f_f is a key feature of these materials, but the influence of ionomer fraction on CO_2 absorption and reactions is yet unknown. In the present study, we will combine the theories of electrospun AEM morphology and CO_2 absorption to predict the effects of CO_2 on electrospun AEM conductivity. The modeling approach provides independent control of key design/operation parameters, which will elucidate their specific role in the system's response to CO_2.

Using an approach previously developed by this project to study CO_2 effects in cast AEM [17] along with a fiber network (FN) model previously developed by this project to describe transport behavior of electrospun AEMs [14], we can now describe electrospun AEM behavior in the presence of CO_2. Specifically, the electrochemical reactions occurring at the electrodes during fuel cell operation result in ionic species fluxes into and out of the membrane, which affect the conversion of OH^- into CO_3^{2-} and HCO_3^-. By applying a species conservation approach using the Nernst-Planck equation, the transient conductivity of the membrane can be calculated as a function operating current, temperature, amount of CO_2 in the cathode gas stream, and other operating parameters. The FN model directly simulates the tortuous, random, 3-D network of ionomer fibers [22]. To integrate the two models, an analytical procedure to map the fibrous morphology to the inputs required by the CO_2 model was created, especially their dependence on f_f. The benefit of this analytical approach is that it is fast and need only be performed once for a certain set of membrane properties, thus enabling the CO_2 model to predict electrospun AEM performance.

The cathode gas stream's CO_2 content is investigated for an electrospun AEM provided by Prof. Peter Pintauro [3]. Figure 8 shows the normalized conductivity loss of the membrane ($1- \sigma/\sigma_{0,f}$) as the cathode CO_2 content is increased. The abscissa indicates the CO_2 content, and the curves are also grouped by different current densities (i – 100, 300, 500 mA/cm^2) as indicated by the labels. The results are banded in groups according to the current density, and within each band are each of the f_f simulated (f_f = 0.4 to 0.9). This demonstrates that the current density is a stronger influence on conductivity loss than the ionomer content of the membrane. As the current density is increased the bands become more tightly grouped which supports this idea.

It is also noteworthy that the cast A201 and ETFE membranes suffer a larger normalized conductivity loss than the electrospun membranes. This is because of the lower IECs of these membranes: a lower IEC means there are fewer native hydroxide ions in the membrane, which makes it more susceptible to CO_2 poisoning. Recall that the main advantages of electrospun AEMs are their higher IECs and water uptakes. Again, however, note that the A201 and ETFE curves approach the bands of electrospun membrane curves as the current density is increased, further supporting the suggestion that morphological parameters become less relevant at higher operating currents. It was found that CO_2 affects electrospun AEMs similarly to cast AEMs, resulting in conductivity loss at low operating currents that is mitigated at higher currents due to the self-purging effect. The volume fraction of ionomer phase f_f can be used to tune electrospun AEM conductivity. However, f_f has a negligible effect on self-purging, probably because conductivity recovery due to self-purging was observed to occur proportionally at the same rate for the range of ionomer content studied.

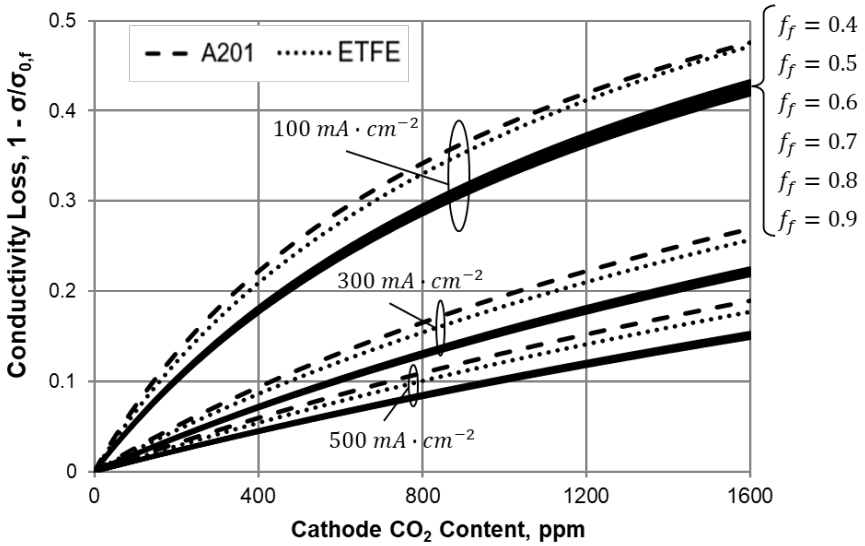


Figure 8. Normalized conductivity loss for an electrospun AEM [3] with different f_f as a function of cathode gas stream CO_2 and current density; cast AEM (Tokuyama A201 [23] and radiation-grafted ETFE [24]) are shown for comparison. Each band of solid curves for the electrospun AEM includes the range of fiber fractions $0.4 \leq f_f \leq 0.9$.

These results were recently presented at the *233rd Electrochemical Society Meeting* (Abstract No. 108354, Seattle, WA, May 13-27, 2018). An additional journal manuscript that discusses the CO_2 effect on electrospun AEM will be submitted in the near future.

7. Analytical Transport Network Model for Rapid Analysis of 3-D Microstructures

A fully analytical, heuristic model – the Analytical Transport Network Model (ATN) – has been created for steady-state, diffusive, potential flow with electrochemical reactions through a 3-D network. Employing a combination of graph theory, linear algebra, and geometry, the model explicitly relates a microstructural network's 3-D topology and the morphology of its channels to an effective material transport coefficient (a general term meant to encompass, e.g., conductivity or diffusion coefficient). The model's transport coefficient predictions agree well with those from comparable established theory, electrochemical fin (ECF) theory and finite element analysis (FEA), but are computed 0.5–1.5 and 5–6 orders of magnitude faster, respectively. In addition, the theory explicitly relates a number of morphological and topological parameters directly to the transport coefficient, whereby the distributions that characterize the structure are readily available for further analysis. Furthermore, ATN's explicit development provides insight into the nature of the tortuosity factor and offers the potential to apply theory from network science and to consider the optimization of a network's effective resistance in a mathematically rigorous manner. The ATN model's speed and relative ease-of-use offer the potential to aid in accelerating the design (with respect to transport), and thus reducing the cost, of energy materials with heterogeneous, functional 3-D microstructure.

Models for steady diffusive flow in energy materials microstructures tend to fall on a spectrum: at one end there are fast, easy to implement, approximate analytical models (heuristic models), and, at the other, slow, more complex, but more accurate numerical models. The former, such as effective medium or percolation theories, are computationally inexpensive, but require significant, simplifying assumptions regarding the microstructure and the relevant physical

phenomena. The latter, e.g., finite element analysis (FEA) and the Lattice Bolzmann Method, can account for multiple processes occurring simultaneously within a geometrically complex domain and tend to be computationally expensive. Models at the simpler end of the spectrum average out local characteristics and, at the more complex end, they are obscured by the techniques' numerical formulation. Ideally, a heuristic model would explicitly account for (1) the properties of the network's material (e.g., transport coefficients); (2) the morphology of the network's channels; and (3) the network's topology. The models currently available, however, tend to greatly simplify morphology and often neglect topology altogether.

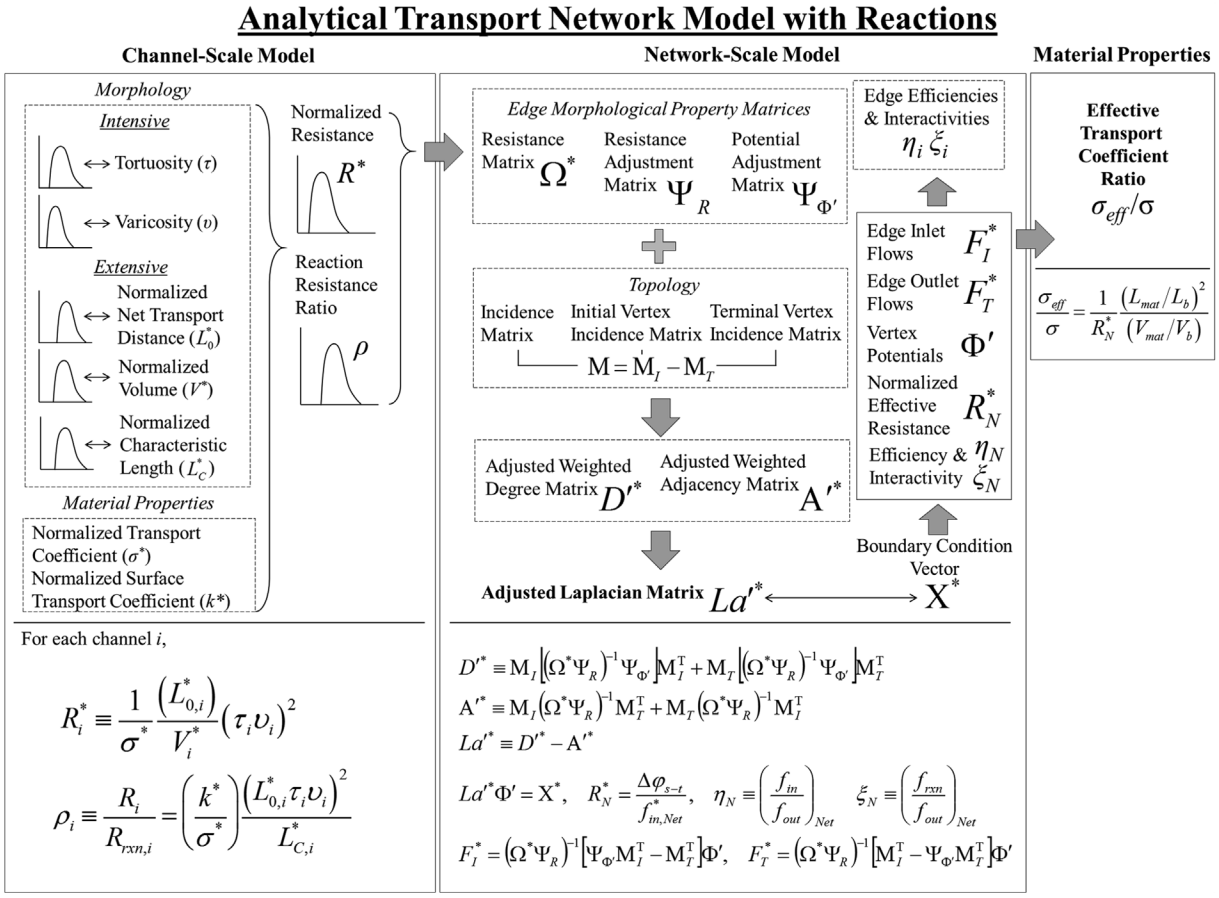


Figure 9. Overview of the Analytical Transport Network (ATN) model for diffusive flow subject to surface reactions that consume flow. Figure is from [25].

The model proposed in this work, ATN, differs from those currently in the literature in two significant ways: (1) it does not assume idealized morphologies for the network's channels (e.g., cylinders, cones, etc.) and (2) using established techniques from graph theory and linear algebra, it explicitly and analytically relates the interplay of local morphology and topology to a microstructural network's resistance, and, in turn, to the effective transport coefficient for the composite containing the network. As with any heuristic model, ATN is approximate, but its speed and explicit analytical development, which results in the definitions of a number of measurable design-relevant metrics shown in Fig. 9, offers a pre-defined point of reference to aid in interpreting experimental measurements and in developing design hypotheses.

Analytical Transport Network is used to predict the effective ionic or electronic conductivity ratio (σ_{eff}/σ) for a subset of the microstructural networks considered in a published comparison of ECF and FEA (using Abaqus). Twenty-six microstructural networks shown in Fig. 10 were considered: 8 artificially generated, mono-sized packed spheres structures and 18 networks from real energy materials that were imaged using x-ray nanotomography. Details of these structures are provided in [26] and its references.

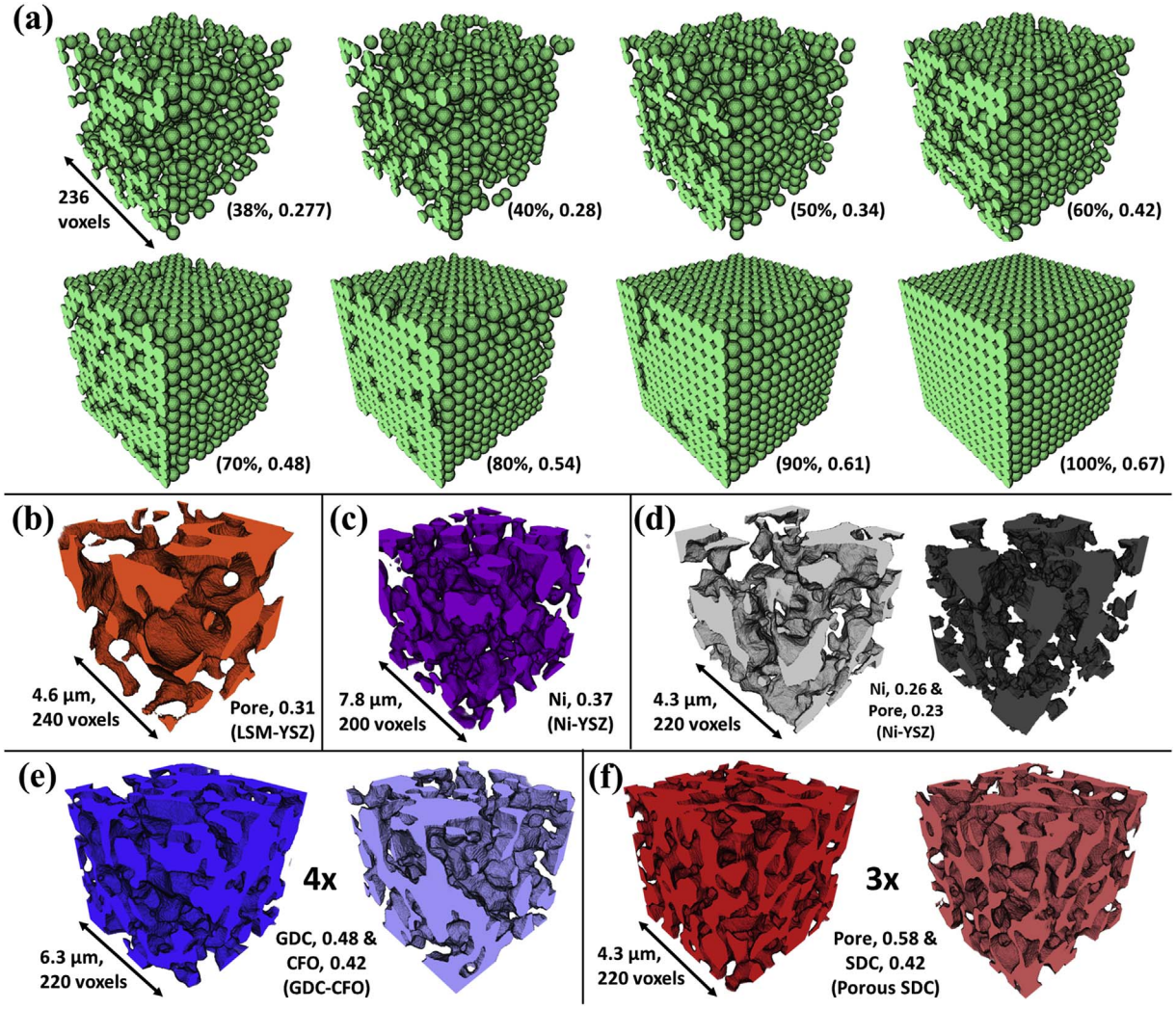


Figure 10. Test structures, with details provided in [26] and its references. (a) Artificially generated, mono-sized packed spheres structures [23]. (b) Pore phase from a porous LSM-YSZ solid oxide fuel cell (SOFC) cathode. (c) Ni network from a Ni-YSZ SOFC anode [45]. (d) Ni and pore networks from the same Ni-YSZ SOFC anode. (e) GDC and CFO networks from GDC-CFO separation membranes. (f) SDC and pore networks from a porous SDC electrode material. In (a), the values in parentheses give the packing percentage and volume fraction of the packed spheres structures. Similarly, the values in (b)–(f) next to the names of the material phases give their respective volume fractions. Figures are from [26].

The σ_{eff}/σ predictions plotted in Fig. 11 show that ATN's predictions agree well with those obtained from FEA (0.014 mean absolute error (MAE)) and ECF (which used spherical fins for the artificial structures and a shape-fitting procedure for the real structures; 0.030 MAE). The model's under-prediction, relative to ECF (0.023 MAE) and FEA (0.035 MAE), of σ_{eff}/σ for many of the real structures is primarily due to under-predictions of the network's inlet and outlet

areas, which resulted from Avizo Autoskeleton Module's tendency (which uses a thinning algorithm) to put a lower density of vertices near the faces of the real structures' volumes. The error is most pronounced for the lowest volume fraction structures. (MAE between ECF and FEA predictions for the packed-spheres and real structures are 0.035 and 0.029, respectively.)

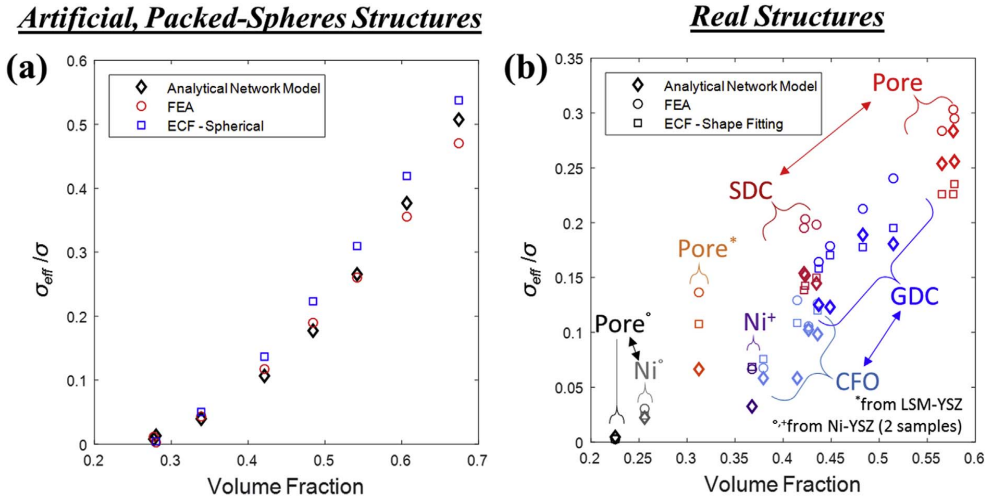


Figure 11. Effective transport coefficient predictions obtained from the ATN model (diamonds), ECF theory (squares), and FEA (circles) for (a) packed spheres and (b) real structures. The markers' colors for the real structures correspond to the colors of their 3-D renderings in Fig. 10. Figures are from [26]

Most important is that ATN captures the data's qualitative trend for both the artificial and real structures. In the case of the real structures, for instance, ATN captures the nonlinear behavior at low volume fraction. The agreement observed for the real structures is particularly good given the relatively simple and uniform approach taken in applying ATN to a diverse set of structures (both ECF and FEA require volume-specific sub-partitioning and meshing considerations that are non-trivial). Reliably capturing qualitative trends is significant in design contexts, for example, when quick, approximate predictions of how a property might change relative to a known benchmark is more important than a stand-alone property prediction; this is the essential value of a heuristic technique like ATN.

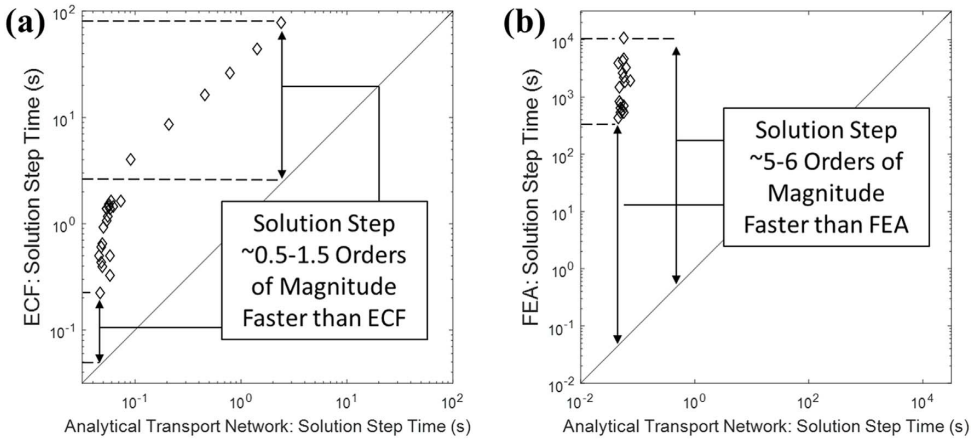
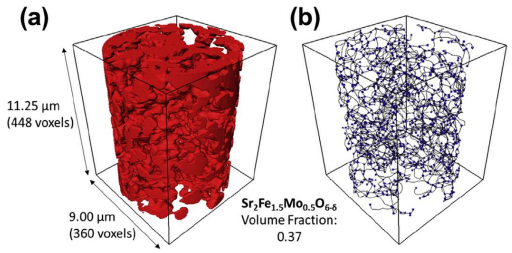


Figure 12. Comparison of computational characteristics. Time for solution step: (a) ATN vs. ECF; and (b) ATN vs. FEA. Figures are from [26].

The computational implementations of ATN, ECF, and FEA are compared in Fig. 12. ATN's solution required approximately 0.5–1.5 and 5–6 orders of magnitude less time than that for ECF and FEA, respectively (Fig. 12a and b). ATN's speed relative to ECF stems from its ability to represent each network with approximately 0.5 orders of magnitude fewer edges and thus fewer vertices. The longest time was 2.5 s for the packed spheres structure with 100% packing and 2018 vertices. The real structures generally had far fewer vertices than the packed spheres structures. As a result, σ_{eff}/σ predictions were obtained more rapidly (tenths of a second for all cases). Then, in addition to requiring much less time for data preparation than ECF and FEA, ATN runs orders of magnitude faster, such that the total time to analyze a given structure is a matter of minutes as opposed to 10's of minutes to hours for ECF and significantly more for FEA.

Reacting-flow ATN was used to analyze electrochemical oxidation of hydrogen and electrochemical reduction of oxygen in SFM ($Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$), a solid oxide fuel cell electrode. This effort will validate Reacting-flow ATN under anodic (in wet hydrogen) and cathodic (in air) conditions reported in [25]. We obtained an imaged SFM volume (Fig. 13a,b) was able to directly compare reacting-flow ATN and ECF predictions with and experimental measurements as shown in Fig. 13, as well as indirectly compare reacting-flow ATN to FEA.



T = 800 °C SFM Vol. Frac. = 0.37	Anode (k/σ) = 440 cm^{-1}	Cathode (k/σ) = 15 cm^{-1}
Experimental Range [Ω cm^2]	0.08–0.80	0.02–0.20
ECF: R_{pol} [Ω cm^2]	0.15	0.019
ATN: R_{pol} [Ω cm^2]	0.51	0.037
ATN: (σ_{eff}/σ)	0.82	0.23
ATN: $\xi_N = (f_{rxn}/f_{in})$	0.95	0.24

Figure 13. (a) 3-D rendering and (b) Skeleton of the SFM (Sr2Fe1.5Mo0.5O6-δ) structure used to compare reacting-flow ATN and ECF. (right) Table comparing reacting flow ATN predictions to ECF predictions and experimental measurements. Figures are from [25].

Reacting-flow ATN was applied to a SFM volume shown in Fig. 13a that is 11.25 µm tall cylindrical with 9 µm diameter, where the transport direction is parallel to the cylinder's height. The sample is at 800 °C, σ = 0.0027 S/cm under anodic conditions and σ = 0.13 S/cm under cathodic. Exchange current densities of i_x = 0.11 A/cm^2 and i_x = 0.18 A/cm^2 were used for the anodic and cathodic conditions. Because all three measurements exhibit sensitivity to material processing and experimental conditions, reported R_{pol} values at a given temperature can vary significantly. Therefore, we compare ECF and ATN estimates against experimental ranges rather than against single values. The results of the comparison are given in Fig. 13. Both the ECF and ATN predictions fall within the, albeit large, experimental ranges for anodic and cathodic conditions. Furthermore, each technique predicts significantly larger R_{pol} under anodic conditions than under cathodic conditions, whereby ATN predictions are significantly larger than those of ECF under each condition. FEA predictions for this comparison under anodic conditions exhibited large charge conservation error (2% vs. 0.03% for ATN) when large computational volumes are considered, which is most likely due to FEA's computational limitations. Therefore, FEA could not be used in this comparison study. In addition, extending the ATN to include reactions was observed to have little impact on the speed of its computer implementation; it remained ~0.5–1.5 and ~5–6 orders of magnitude faster than ECF and FEA analyses.

This effort has resulted in the publication of two journal articles in the *Journal of Power Source* [25], [26], a conference presentation at the *232nd Electrochemical Society Meeting* (Abstract No. 105132, National Harbor, MD, October 1-6, 2017; *ECS Trans.*, 80, 2017), and a conference presentation at the *233rd Electrochemical Society Meeting* (Abstract No. 108886, Seattle, WA, May 13-27, 2018).

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