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Final Report: Electrochemical Impedance Spectrometer with an Environmental Chamber for Rapid Screening of New Precise Copolymers

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W911NF-14-1-0466

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13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

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a. REPORT	b. ABSTRACT	c. THIS PAGE			KAREN WINEY
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RPPR Final Report
as of 12-Oct-2017

Agency Code:

Proposal Number: 65220CHRIP **Agreement Number: W911NF-14-1-0466**
INVESTIGATOR(S):

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DUNS Number: 042250712 EIN: 231352685
Report Date: 14-Dec-2016 Date Received: 07-Oct-2017
Final Report for Period Beginning 15-Aug-2014 and Ending 14-Sep-2016
Title: Electrochemical Impedance Spectrometer with an Environmental Chamber for Rapid Screening of New Precise Copolymers
Begin Performance Period: 15-Aug-2014 **End Performance Period:** 14-Sep-2016
Report Term: 0-Other
Submitted By: KAREN WINEY Email: winey@seas.upenn.edu
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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1 **STEM Participants:** 5

Major Goals: Advances in batteries, fuel cells, and permselective membranes are materials limited. New acid- and ion-containing polymers must be designed and synthesized to deliver improved combinations of mechanical toughness, transport selectivity and ionic conductivity. A formidable obstacle toward producing the next generation of polymer membranes is the fundamental understanding of how chemical structure and polymer processing impact the morphology that subsequently dictates ionic conductivity.

In 2007, a new class of acid-containing polymers was synthesized using acylic diene metathesis polymerization to make linear polyethylenes with carboxylic acid groups at precise intervals along the polymer. Precise acid-containing polymers provide unprecedented control over polymer morphology and produce new well-defined superstructures. We have access to these materials and through the world-class facilities at Penn we have access to various instruments for morphological characterization. However, our access to impedance spectroscopy is limited and, consequently, our scientific progress will be hampered.

The primary objective of our ARO grant is to rapidly screen precise acid copolymers to identify polymers and morphologies with significantly improved ionic conductivity. Thus, this proposal requests an electrochemical impedance spectrometer within an environmental chamber to measure the ionic conductivity of precise copolymers and their ionomers across various conditions.

Having an electrochemical impedance spectrometer in our lab will accelerate our property measurements of these novel and promising polymers. Rapid feedback between our various fabrication methods to alter the polymer morphology and evaluating the impact of these morphological changes on ion conductivity is essential. This will be particularly important as we endeavor to orient polymer crystallization and thereby align morphologies to provide continuous ion pathways through the membrane for increased ionic conductivity. In addition, the students working on this project will develop a better understanding of EIS by logging more hours on the instrument and by developing LabVIEW code to integrate and automate data collection

Accomplishments: The electrochemical impedance spectrometer, cryostat and environmental chamber has been purchased and installed. A LabVIEW code has been written in house to control the instrument, which allows for the cryostat and the environmental chamber to be used at the same time. We have designed and tested a variety of electrode geometries to accommodate a variety of samples from compression modeled films (~ 50 - 100 microns thick) to thinner solution cast films. A standard operating procedure has been written. To date, 1 postdoc, 3 graduate students, and 2 undergraduate student have become independent users on the instrument.

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The instrument has been integral to our study of ion conductivity in polymers, particularly a precise sulfonic acid polyethylene and the a polymerized ionic liquids based on cyclopropenium. The instrument is also be used to study polymer segmental dynamics in polymer nanocomposites (bulk and thin films).

At present, three manuscripts are in preparation.

Training Opportunities: Nothing to Report

Results Dissemination: At present, three manuscripts are in preparation.

Honors and Awards: Trustees Council of PennWomen Award for Undergraduate Advising, 2017

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

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

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Phillip Griffin
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: Edward Trigg
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: Benjamin Paren
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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Participant Type: Graduate Student (research assistant)
Participant: Eric Bailey
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Eric Schwartz
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
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Person Months Worked: 3.00 **Funding Support:**
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International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

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Volume: Issue: First Page #:
Date Submitted: 10/7/17 12:00AM Date Published:
Publication Location:
Article Title: The Impact of Electronic Structure on the Anomalous Ion Transport Behavior of Cyclopropenium-Based Polyelectrolytes
Authors: Philip J. Griffin, Jessica L. Freyer, Nicholas Han, Noah Geller, Xiaodong Yin, Chirag D. Gheewa-la, Trist
Keywords: polymerizes ionic liquids, ion conductivity
Abstract: Broadband dielectric spectroscopy (BDS) and temperature modulated DSC was performed on novel polymerized ionic liquids containing a pendant trisaminocyclopropenium ion. This electron rich cation has a highly delocalized. Ionic conductivity was measured for three counterions: chloride (Cl), bis(trifluoromethane) sulfonamide (TFSI), and pentacarboxycyclopentadienyl (CPDE). Interestingly, the polymer with Cl- exhibited counterion motion that is decoupled from the polymer dynamics.
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Volume: Issue: First Page #:
Date Submitted: 10/7/17 12:00AM Date Published:
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Article Title: Segmental Diffusion in Highly-Attractive Polymer Nanocomposites: A Quasi-Elastic Neutron Scattering Study
Authors: Eric J. Bailey, Philip J. Griffin, Vera Bocharovas, Madhusudan Tyagi§, Karen I. Winey
Keywords: polymer nanocomposites, QENS, BDS
Abstract: We study the segmental dynamics in model highly attractive polymer nanocomposites using quasi-elastic neutron scattering (QENS) and broadband dielectric spectroscopy. We show that on accessible length and time scales, poly(2-vinylpyridine) (P2VP) segments exhibit classic translational diffusion, even in the presence of 50 vol% well-dispersed silica nanoparticles (NPs). However, the average segmental diffusion coefficient decreases with increasing NP loading, up to 80% relative to bulk, and is nominally independent of temperature. By comparing an unentangled matrix to a well-entangled matrix, we also show that the reduction in diffusion coefficient is slightly larger at lower molecular weights. By comparing to different measurements on similar material systems, we highlight the importance of considering critical details regarding techniques and measurement conditions before making similar comparisons.
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Article Title: Proton Transport through Polymer Crystals: Lamellar Water Channels in Chain-Folded Precisely Sulfonated Polyethylene
Authors: Edward B. Trigg, Taylor W. Gainesb, Mark J. Stevens, Manuel Marechal, Demi E. Moed, Hakima Mendi
Keywords: proton transport, precise polymer, atomistic molecular dynamics
Abstract: Here we demonstrate well-controlled chain folding of sulfonated polyethylene at a length scale of 2.5 nm to produce a highly uniform morphology with high proton conductivity. The linear polyethylene contains sulfonic acid groups pendant to precisely every 21st carbon atom, and the acid groups induce tight chain folds upon crystallization of the alkyl segments. Many consecutive alternating layers of crystalline alkyl segments and hydrated acid groups are formed, with periodicity ~ 2.5 nm. The proton conductivity through these layers is on par with Nafion 117, the industry standard for fuel cell membranes. This is the first time, to our knowledge, that controlled polymer folding has been utilized for proton or ion transport, and the first time high proton conductivity has been reported within a crystalline polymer. The simplicity of the polymer's chemical structure and morphology is a significant achievement in the control of structure for producing desired properties.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Nothing to report in the uploaded pdf (see accomplishments).