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14. ABSTRACT

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a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 215-898-0593

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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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

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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 acyclic 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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as of 12-Oct-2017

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

Participant: Nicholas Han

Person Months Worked: 3.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

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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, Tristram

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.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

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