REPORT DOCUMENTATION PAGE

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23-05-2023	Final Report	1-May-2015 - 31-Aug-2019

4. TITLE AND SUBTITLE

Final Report: Fundamental Studies on the Dynamics and Energetics of Protic Ionic Liquids, and Some Applications to Fuel Cells

5a. CONTRACT NUMBER
W911NF-15-1-0137

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

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12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for public release; distribution is unlimited.

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

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Charles Angell
UU	UU	UU	UU		19b. TELEPHONE NUMBER 480-965-7217

RPPR Final Report
as of 25-May-2023

Agency Code: 21XD

Proposal Number: 66682ES **Agreement Number: W911NF-15-1-0137**
INVESTIGATOR(S):

Name: Charles Austen Angell
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DUNS Number: 943360412 EIN: 860196696

Report Date: 30-Nov-2019 Date Received: 23-May-2023
Final Report for Period Beginning 01-May-2015 and Ending 31-Aug-2019
Title: Fundamental Studies on the Dynamics and Energetics of Protic Ionic Liquids, and Some Applications to Fuel Cells
Begin Performance Period: 01-May-2015 **End Performance Period:** 31-Aug-2019
Report Term: 0-Other

Submitted By: Waunita Parrill Email: wparrill@asu.edu
Phone: (000) 000-0000

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

STEM Degrees: **STEM Participants:**

Major Goals: This effort seeks to characterize new superprotonic ionic liquids, high acidity at low ionicity, inorganic protic ionic liquids and basic and superbasic ionic liquids.

Accomplishments: Results of the research performed during the past year have been disseminated in a variety of ways. First there are the published works, which are collected in the first section of the attached report, as stipulated. The past year has seen three new papers from this group, one of them based on a plenary lecture invited for the 15th International Symposium on Polymer Electrolytes, held in Uppsala Sweden in August of 2016. The lecture consisted of (teaching) component, and a novel research component in which we incorporated recently published work on our all-inorganic flexible solid fuel cell membrane. The dissemination via oral presentations at international conferences has proven one of the best dissemination routes. During the past year, (then student Hasani gave an oral presentation of his work on acid classification at the PACRIM meeting Electrochem meeting in Hawaii, and student Iolanda Klein gave a well-received presentation of her new superprotonic and superionic solid electrolytes at the Fall MRS meeting in Phoenix, while PI Angell gave invited tutorial presentations and research talks on electrolytes at the same meeting. He also gave an invited talk in the symposium ES13 of the spring(April 2017) MRS meeting in Phoenix. Under the title : Ultraconcentrated "Solutions" for Alkali Metal and Multivalent Energy Storage Electrolytes—Common Features and Ionicities" incorporating some of ex-student Hasani's results.

Training Opportunities: Nothing to Report

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

ARTICLES:

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as of 25-May-2023

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry B
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpcb.6b01203
Volume: 120 Issue: 18 First Page #: 4279
Date Submitted: 9/13/16 12:00AM Date Published: 5/1/16 7:00AM
Publication Location: Phoenix, AZ
Article Title: NMR Characterization of Ionicity and Transport Properties for a Series of Diethylmethylamine Based Protic Ionic Liquids
Authors: Stephen K. Davidowski, Forrest Thompson, Wei Huang, Mohammad Hasani, Samrat A. Amin, C. Austei
Keywords: NMR Characterization, Ionicity and Transport Properties, Diethylmethylamine, Ionic Liquids
Abstract: The ionicity and transport properties of a series of diethylmethylamine (DEMA) based protic ionic liquids (PILs) were characterized, principally utilizing nuclear magnetic resonance (NMR) spectroscopy. PILs were formed via the protonation of DEMA by an array of acids spanning a large range of acidities. A correlation between the 1H chemical shift of the exchangeable proton and the acidity of the acid used for the synthesis of the PIL was observed. The gas phase proton affinity of the acid was found to be a better predictor of the extent of proton transfer than the commonly used aqueous ?pKa. Pulsed field gradient (PFG) NMR was used to determine the diffusivity of the exchangeable proton in a subset of the PILs. The exchangeable proton diffuses with the acid if the PIL is synthesized with a weak acid, and with the base if a strong acid is used. The ionicity of the PILs was characterized using the Walden analysis and by comparing to the ideal Nernst?Einstein conductivity predicted . . .
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemistry - A European Journal
Publication Identifier Type: DOI Publication Identifier: 10.1002/chem.201601428
Volume: 22 Issue: 37 First Page #: 13312
Date Submitted: 9/13/16 12:00AM Date Published: 9/1/16 7:00AM
Publication Location: Phoenix, AZ
Article Title: On the Use of a Protic Ionic Liquid with a Novel Cation To Study Anion Basicity
Authors: Mohammad Hasani, Jeffery L. Yarger, C. Austen Angell
Keywords: Protic Ionic Liquid, Novel Cation, Anion Basicity
Abstract: The need for reliable means of ordering and quan- tifying the Lewis basicity of anions is discussed and the cur- rently available methods are reviewed. Concluding that there is need for a simple impurity-insensitive tool, we have sought, and here describe, a new method using NMR spec- troscopy of a weak base, a substituted urea, 1,3-dimethyl-2- imidazolidinone (DMI), as it is protonated by Brønsted acids of different strengths and characters. In all cases studied the product of protonation is a liquid (hence a protic ionic liquid). NMR spectroscopy detects changes in the electronic structure of the base upon interaction with the proton donors. As the proton-donating ability, that is, acidity, in- creases, there is a smooth but distinct transition from a hy-drogen-bonded system (with no net proton transfer) to full ionicity. The liquid state of the samples and high concentra- tion of nitrogen atoms, despite the very low natural abun- dance of its preferred NMR-active isotope (15N), ...
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

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as of 25-May-2023

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
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Publication Identifier Type: DOI Publication Identifier: 10.1016/j.jpowsour.2015.10.034
Volume: 303 Issue: First Page #: 142
Date Submitted: 9/15/16 12:00AM Date Published: 1/1/16 7:00AM
Publication Location: Phoenix, AZ
Article Title: A flexible all-inorganic fuel cell membrane with conductivity above Nafion, and durable operation at 150 °C
Authors: Y. Ansari, T.G. Tucker, W. Huang, I.S. Klein, S.-Y. Lee, J.L. Yarger, C.A. Angell
Keywords: Inorganic fuel cell membrane conductivity above nafion, 150 C fuel Cell
Abstract: The search for fuel cell membranes has focused on carbon backbone polymers, among which Nafion seems to best survive the most severe of the degradation mechanisms e attack by peroxide radicals. Less attention has been given to inorganic membranes because of their generally inflexible nature and lower conductivity, though some SiO2-Nafion composites have shown improved properties. Nafion dominates, despite needing hydration, which then restricts operation to below 100 C (so CO poisoning problems persist). Described herein is a low cost, flexible, and all-inorganic fiberglass reinforced gel membrane with conductivity exceeding that of Nafion at any temperature above 60 C. Using Teflon fuel cells, maximum currents > 1 Acm 2 and OCV of 1.03 V at 150 C are demonstrated. No detectable loss of cell potential was observed over 24 h during 50 mAcm 2 constant current operation at 120 C while, at 150 C and maximum power, the degradation rate is intermediate among other high conductivity H3PO
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: J. Mater. Chem. A
Publication Identifier Type: Publication Identifier: 10.1039/C6TA10956J
Volume: 5 Issue: 27 First Page #: 14092
Date Submitted: Date Published:
Publication Location: Phoenix, AZ
Article Title: Silicon hydrogensulfates: solid acids with exceptional 25 °C conductivities and possible electrochemical device applications
Authors: I. S. Klein, S. K. Davidowski, J. L. Yarger, C. A. Angell
Keywords: solid acids, acid catalysis, exotic protonation
Abstract: Solid acids as a class are of much interest in areas such as acid catalysis, and exotic protonation chemistries. They include the strongest acids yet identified. A subclass exhibit very high protonic conductivity and its members have been investigated as possible fuel cell electrolytes, as first demonstrated by Haile's group in 2001 with CsHSO4. These superprotonic plastic crystals bring a "true solid state" alternative to polymer electrolytes, operating at mild temperatures (150-200oC) without the requirement of humidification. However, they suffer from the narrow operating temperature range, and other problems. Here we describe a new class of solid acids based on silicon, which are of general interest. Its members have extraordinary conductivities, as high as 21.5 mS/cm at room temperature, orders of magnitude above any previous reported case. We discuss possible applications. Although the present electrolytes are not suitable for H2/O2 fuel cell applications due to hydrolizable comp
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 25-May-2023

Partners

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I certify that the information in the report is complete and accurate:
Signature: Hugh Delong
Signature Date: 5/23/23 5:22PM

ROUTING AND ACTION MEMORANDUM

ROUTING

TO: Energy Sciences Branch (ES) Division
(DeLong, Hugh)

Proposal Number 66682-ES-

After signing, please return this sheet to the ARO Information Management Office.

DESCRIPTION OF MATERIAL

CONTRACT OR GRANT NUMBER: W911NF1510137
INSTITUTION: Arizona State University
ORSPA
P.O. Box 876011
Tempe, AZ 85287-6011
UNITED STATES

PRINCIPAL INVESTIGATOR: Dr. Charles Austen Angell

TYPE REPORT: Final Report was Due November 30, 2019
plus previous interim report Period Covered (if applicable):

TITLE: Fundamental Studies on the Dynamics and Energetics of Protic Ionic Liquids, and Some Applications to Fuel Cells

ACTION TAKEN BY DIVISION

( ) Unavailability of the Principal Investigator prevents the registering of a formal final report. Progress as detailed in the Interim Progress Reports was considered to be satisfactory.

( ) Unavailability of the Principal Investigator necessitates closing the agreement without the final technical report.

(X) Other: PI has died and his assistant has left university, so we can't get anymore reports from him.

DELONG.HUGH.C.1037605251 Digitally signed by DELONG.HUGH.C.1037605251
Date: 2023.05.23 16:13:16 -04'00'

(Signature) (Date)

ARO FORM 36-E
15 Mar 89