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4. TITLE AND SUBTITLE Femtosecond Broad-Band Sum Frequency Generation Spectroscopy: Measurements of Ethanol Fuel Cell Catalysis			5a. CONTRACT NUMBER W911NF-08-1-0309		
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			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Dana D. Dlott, Andrzej Wieckowski			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Illinois - Urbana OSPRA The Board of Trustees of the University of Illinois Champaign, IL 61820 -7406			8. PERFORMING ORGANIZATION REPORT NUMBER		
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14. ABSTRACT This is a fundamental science project relevant to ethanol fuel cells (DEFCs). We studied ethanol electrooxidation (EOR) on polycrystalline platinum in acidic and alkaline media. The method used was the broadband sum-frequency generation (BB-SFG) spectroscopy that we connected to the solid/liquid interfacial research for the first time. In both alkaline and acidic media we monitored oxidation of isotopically labeled ethanol ((12)CH(3)-(13)CH(2)OH). Surface-adsorbed (12)CO and (13)CO were observed and showed different potential-dependent					
15. SUBJECT TERMS Ethanol, BB-SFG, catalysis, acidic media, alkaline media, new surface radical, Co-porphyrines (macrocycles)					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Andrzej Wieckowski
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Report Title

Femtosecond Broad-Band Sum Frequency Generation Spectroscopy: Measurements of Ethanol Fuel Cell Catalysis

ABSTRACT

This is a fundamental science project relevant to ethanol fuel cells (DEFCs). We studied ethanol electrooxidation (EOR) on polycrystalline platinum in acidic and alkaline media. The method used was the broadband sum-frequency generation (BB-SFG) spectroscopy that we connected to the solid/liquid interfacial research for the first time. In both alkaline and acidic media we monitored oxidation of isotopically labeled ethanol ((¹²)CH(³)-(¹³)CH(²)OH). Surface-adsorbed (¹²)CO and (¹³)CO were observed and showed different potential-dependent behaviors. The ¹²CO showed evidence of methyl-like species formation (–¹²CH_x) that was difficult to oxidize to CO₂; the ¹²CH_x was found not to be oxidatively removed until the electrode potential was swept past 0.65 V. In sulfuric acids the results included adsorbed acetate and co-adsorbed sulfuric acid anions. For the DEFC cathode, the Co-OEP macrocycle was chosen and characterized with both Raman and BBSFG spectroscopies. The emphasis was given to V11 transition at 1577 cm⁻¹, as this band shifted in frequency as the transition metal center was changed. There is no Stark tuning effect associated with the Co-OEP macrocycle adsorption.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
08/24/2011	1.00 Björn Braunschweig, Prabuddha Mukherjee, Rachel L. Behrens, Dana D. Dlott, Andrzej Wieckowski, Robert B. Kutz. Reaction pathways of ethanol electrooxidation on polycrystalline platinum catalysts in acidic electrolytes, Journal of Catalysis, (03 2011): 181. doi: 10.1016/j.jcat.2010.11.018
08/24/2011	2.00 Bjo?rn Braunschweig, Prabuddha Mukherjee, Robert B. Kutz, Andrzej Wieckowski, Dana D. Dlott. Sum-frequency generation of acetate adsorption on Au and Pt surfaces: Molecular structure effects, The Journal of Chemical Physics, (12 2010): 234702. doi: 10.1063/1.3507257
08/24/2011	3.00 Bjo?rn Braunschweig, Prabuddha Mukherjee, Dana D. Dlott, Andrzej Wieckowski. Real-Time Investigations of Pt(111) Surface Transformations in Sulfuric Acid Solutions, Journal of the American Chemical Society, (10 2010): 14036. doi: 10.1021/ja106618z
08/24/2011	4.00 Robert B. Kutz, Bjo?rn Braunschweig, Prabuddha Mukherjee, Dana D. Dlott, Andrzej Wieckowski. Study of Ethanol Electrooxidation in Alkaline Electrolytes with Isotope Labels and Sum-Frequency Generation, The Journal of Physical Chemistry Letters, (08 2011): 0. doi: 10.1021/jz200957e
10/26/2011	5.00 Aaron Lozano, Prabuddha Mukherjee, Selezion A. Hambir, Alexei Lagutchev, Dana D. Dlott. Compact broadband vibrational sum-frequency generation spectrometer with nonresonant suppression, Spectroscopica Acta part A, (04 2010): 1286. doi: 10.1016/j.saa.2009.12.066
12/02/2012	13.00 David Hibbitts, Matthew Neurock, Bjoern Braunschweig, Andrzej Wieckowski. Electrocatalysis: A direct alcohol fuel cell and surface science perspective, Catalysis Today, (10 2012): 0. doi:
TOTAL:	6

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. (invited) ACS Colloids and Surface Chemistry Symposium, Columbia University, June 2009, "Vibrational dynamics at interfaces probed by vibrational sum-frequency generation spectroscopy".
2. (invited) Gordon Conference on Vibrational Dynamics at Surfaces, Proctor Academy, Andover, NH, Aug. 2009, "Dynamics at interfaces probed by time-resolved sum-frequency spectroscopy".
3. (invited) Army Research Office Review of Nano-engineered energetic materials, Aberdeen, MD, Mar. 2010, "Ultrafast dynamics of NEEMs".
4. (invited) "Molecular transformations and energy transfer at interfaces", USC-DOE conference on "Materials for Energy Applications - Experiment, Modeling and Simulations", Mar. 2011, Los Angeles, CA.
5. (invited) Air Force Office of Scientific Research Molecular Dynamics Meeting, Pasadena, CA, May 2011, "Nonlinear coherent vibrational spectroscopy in electrochemical surface science and electrocatalysis"
6. (invited) Studium Conference on in situ molecular spectroscopic technique and application, Orleans, France, June 2011, "In situ probing by time-resolved vibrational spectroscopy: shocked materials and energy storage media"
7. (invited) American Chemical Society National Meeting, Denver, CO Aug. 2011, "Interfaces under extreme conditions"
8. (invited) "Interfaces under extreme conditions", Oct. 2011, Rice University Department of Chemistry
9. (invited) "Nonlinear coherent vibrational spectroscopy of electrochemistry", Xiamen University Department of Chemistry, Xiamen, P. R. China, Feb. 2012.
10. (invited) "Nonlinear coherent vibrational spectroscopy of electrochemical transformations", American Chemical Society National Meeting, Philadelphia, PA Aug. 2012.
11. (invited) The Nanyang Technological University (NTU), "Broad-Band Vibrational Sum Frequency Generation of Surface CO on Pt(hkl) Electrodes", Singapore, August 7, 2008.
12. (invited) 235th ACS National Meeting, "The Power of Broad-Band Sum Frequency Generation", Philadelphia, PA, August 19, 2008.
13. (invited) The ISE International Meeting, Seville, Spain, "Update on the Use of BB-SFG in Electrochemical Research", September 10, 2008.
14. (invited) Chemistry Department of the Warsaw University, Poland: "Vibrational BB-SFG Applied to Study of Electrochemical Interfaces", March 20, 2009.
15. (invited) Warsaw Technical University, Warsaw, Poland, "Fuel Cell Lectures and Seminars", March 27 – April 3, 2009.
16. (invited) The International Society of Electrochemistry, "The Use of Spectroscopy in Research on Electrocatalysis and Fuel Cell Catalysis" ISE 60th, Beijing, August 16-21, 2009.
17. (invited) Materials Research Society Meeting, "Small Molecule Decomposition on Catalytic Electrodes by the use of Vibrational BB-SFG and Electrochemistry", Boston, Massachusetts, November 29 - December 4, 2009.
18. (invited) ACS Meeting, San Francisco, CA, "BB-SFG and Electrochemistry of Ethanol Intermediates in Acidic and Basic Media", March 21-25, 2010.
19. (invited) A lecture given during 2010 Electrochemistry GRC involving focus on BB-SFG, January 10 - 15, 2010.
20. (invited) CECAM conference on quantum electrochemistry, "BB-SFG and Electrochemistry of Ethanol Intermediates in Acidic and Basic Media", Lausanne Switzerland, July 12-14, 2010.
21. (invited) International Symposium on Portable Fuel Cells, November 3-5, 2010, Changxing, China, "Broadband Sum-Frequency

Generation of Ethanol Oxidation Intermediates in Acidic and Basic Electrolytes on Platinum".

22. (invited) USA-Poland Consultations on Science and Technology, Warsaw, Poland, May 20-21, 2010.

23. (invited) WPI-AIMR Annual Workshop, "An Update on the Application of Broad Band Sum Frequency Generation for Studies of Electrode Adsorption", Sendai, Japan, February 21-24, 2011.

24. (invited) 43rd IUPAC World Chemistry Congress, "Broad Band Sum Frequency Generation for Studies of Ethanol Adsorption on Platinum in Basic Media", St. Juan, PR, August 1, 2011.

25. (invited) Materials of 220th Meeting of ECS, "Broad Band Sum Frequency Generation, Boston MA, October 9-14, 2011.

26. (organized) 2012, May 6-10, Seattle, WA - 221st Meeting; symposium on spectro-electrochemistry organized.

27. (invited) 2012, May 27 – June 1st; Jerzy Haber Institute of Catalysis and Surface Chemistry, Krakow, Poland; "Oxygen Reduction Reaction by Porphyrin-Based N4 Macrocycles Catalysts for Fuel Cells".

Number of Presentations: 27.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
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09/26/2012	10.00	. Enhanced ORR Activity of Cobalt Porphyrin Co-deposited with Transition Metal Oxides on Au and C Electrodes, Electrochemistry Communications (12 2012)
12/02/2012	14.00	Niancai Cheng, Robert Kutz, Christopher Kemna, Paul S. Bagus, Andrzej Wieckowski. Enhanced ORR Activity of Cobalt Porphyrin Co-deposited with Transition Metal Oxides on Au and C Electrodes, Electrochemistry Communications, to be submitted (01 2013)
TOTAL:		2

Number of Manuscripts:

Books

<u>Received</u>	<u>Paper</u>
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09/24/2012	6.00	G. Q. Lu, A. Lagutchev, T. Takeshita, R. L. Behrens, D. D. Dlott , A. Wieckowski . "Broad-Band Sum Frequency Generation Studies of Surface Intermediates Involved in Fuel Cell Electrocatalysis", Hoboken, New Jersey: John Wiley & Sons, Inc. , (11 2009)
12/03/2012	15.00	Björn Braunschweig, Prabuddha Mukherjee, Robert B. Kutz, Armin Rumpel , Kathrin Engelhardt, Wolfgang Peukert, Dana D. Dlott, Andrzej Wieckowski. Spectroscopy of Electrified Interfaces with Broadband Sum-Frequency Generation: From Electrocatalysis to Protein Foams, New Jersey: Book chapter, (03 2013)
TOTAL:		2

Patents Submitted

20060210867; Membraneless electrochemical cell and microfluidic device without pH constraint.

20030198852; Fuel cells and fuel cell catalysts.

Patents Awarded

Licensed to LANL, New Mexico:

S-118967 : 2010 "Chalcogen Catalysts for Polymer Electrolyte Fuel Cells." This patent covers the catalyst itself and a method of making MEA using the catalyst.

Awards

Gold Medal of the International Society of Electrochemistry (ISE), 2007

DDD: William H. and Janet G. Lycan Professor of Chemistry at UIUC, 2009

AW: Fellow of ISE (the International Society of Electrochemistry), 2009

Chair APS Topical Group on Shock Compression of Condensed Matter, 2008

External Review Panel, Los Alamos National Laboratory LDRD, Apr. 2008.

Jupiter Laser Facility Program Advisory Committee, Lawrence Livermore National Laboratory, 2008

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Rachel Lynn Behrens	0.50	
Robert Brien Kutz	0.50	
FTE Equivalent:	1.00	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Bjoern Braunschweig	0.50
Prabuddha Mukherjee	0.20
FTE Equivalent:	0.70
Total Number:	2

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
A.Wieckowski	0.10	
D. D. Diott	0.05	
FTE Equivalent:	0.15	
Total Number:	2	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Thomas Takeshita	0.00	of Japan
FTE Equivalent:	0.00	
Total Number:	1	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	2.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:	1.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
None
Total Number:

1

Names of personnel receiving PhDs

NAME

Rahel Lynn Beherens

Robert Brien Kutz

Total Number: 2

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

This is a fundamental science project relevant to ethanol fuel cells (DEFCs). The main project accomplishments is evidence towards methyl-like species formation (-12CH_x) during ethanol decomposition on platinum. This may be the stable surface intermediate that discriminates between methanol and ethanol oxidation. We explained why it is better to use alkaline media (than acidic media) to oxidize ethanol (0.2 V difference in activating ethanol between the two media). We have studied adsorbed CO and formic acid; the study of CO is complete. We identified the formate as one of the adsorbate components of HCOOH, in support of work by Osawa et al. The major contribution to science during the last project year is also the study of DEFC cathode (or fuel cells in general and for DE). The Co-OEP macrocycle was chosen (due to earlier NSF supported results), and characterized with both Raman and BBSFG spectroscopies (reactivity vs. characterization). Particular emphasis was given to the V11 transition at 1577 cm^{-1} , as this band shifted in frequency as the transition metal center is changed. Changing the applied potential did not change the observed BB-SFG frequencies, and we conclude that there is no Stark tuning effect associated with Co-OEP macrocycle adsorption (as a cathode of DEFC fuel cell). We have concluded that BB-SFG is a powerful tool for in-situ observation of key molecular vibrations.

Technology Transfer