

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 10-10-2015		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 15-Aug-2014 - 14-Nov-2014	
4. TITLE AND SUBTITLE Final Report: Potentiostat for Characterizing Microstructures at Ionic Liquid/Electrode Interfaces			5a. CONTRACT NUMBER W911NF-14-1-0547		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Luke Haverhals			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Bradley University 1501 W. Bradley Ave. Peoria, IL 61625 -0003			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 66259-CH-RI.1		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT This report details the procurement and integration of a multichannel potentiostat (BioLogic VMP 16 Channel Potentiostat) into our electrochemistry program. In short, the instrument has been of great service to characterize ionic liquid-based (IL-based) electrolyte systems via simultaneous electrochemical and spectroscopic studies. These data are pertinent to understanding the microscopic (molecular and ionic) dynamics of electrolyte/electrode interfaces. This information that is a prerequisite to engineered progress of many important energy conversion processes and devices (e.g., supercapacitors). The potentiostat has been synchronized with an infrared spectrometer.					
15. SUBJECT TERMS Ionic Liquids Electrochemistry					
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT	b. ABSTRACT			c. THIS PAGE	Luke Haverhals
UU	UU	UU		19b. TELEPHONE NUMBER 309-677-4862	

Report Title

Final Report: Potentiostat for Characterizing Microstructures at Ionic Liquid/Electrode Interfaces

ABSTRACT

This report details the procurement and integration of a multichannel potentiostat (BioLogic VMP 16 Channel Potentiostat) into our electrochemistry program. In short, the instrument has been of great service to characterize ionic liquid-based (IL-based) electrolyte systems via simultaneous electrochemical and spectroscopic studies. These data are pertinent to understanding the microscopic (molecular and ionic) dynamics of electrolyte/electrode interfaces. This information that is a prerequisite to engineered progress of many important energy conversion processes and devices (e.g., supercapacitors). The potentiostat has been synchronized with an infrared spectrometer to perform surface enhanced infrared absorption (SEIRA) spectroscopy with electrochemical control. The multichannel instrument has also been utilized to study mass transport in mesoporous films. Sample data from these ongoing efforts are demonstrated later in this report.

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>
-----------------	--------------

TOTAL:

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>
-----------------	--------------

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

C. Zibart, D. Parr, B. Egan, H. Morris, A. Tivanski, L. M. Haverhals, "Investigation of Structure at Gold-Ionic Liquid Electrolyte Interfaces", Argonne National Laboratory 24th Annual Undergraduate Symposium, 7 November, 2014, Argonne, Illinois.

C. Meunier, E. Roberts, E. Remsen, L. M. Haverhals, "Investigation of Mass Transport in Mesoporous Semiconducting Thin Film Electrodes", Argonne National Laboratory 24th Annual Undergraduate Symposium, 7 November, 2014, Argonne, Illinois.

C. Zibart, B. Egan, and D. Parr, H. Morris, Alexei Tivanski, L. M. Haverhals, "Microstructure at the Ionic Liquid/Electrode Interface", 226th ECS Meeting, 8 October, 2014, Cancun, Mexico.

Number of Presentations: 3.00

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

Received Paper

TOTAL:

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

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

Received Paper

TOTAL:

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

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Post Doctorates

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

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: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

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):..... 0.00

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>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

See Attachment

FINAL REPORT

“Potentiostat for Characterizing Microstructures at Ionic Liquid/Electrode Interfaces”

**Proposal #: 66259CHRI
Agreement #: W911NF1410547
08/15/2014 – 11/14/2014**

**Prepared by: Luke Haverhals
Assistant Professor
Department of Chemistry
Bradley University**

Abstract

This report details the procurement and integration of a multichannel potentiostat (BioLogic VMP 16 Channel Potentiostat) into our electrochemistry program. In short, the instrument has been of great service to characterize ionic liquid-based (IL-based) electrolyte systems via simultaneous electrochemical and spectroscopic studies. These data are pertinent to understanding the microscopic (molecular and ionic) dynamics of electrolyte/electrode interfaces. This information that is a prerequisite to engineered progress of many important energy conversion processes and devices (e.g., supercapacitors). The potentiostat has been synchronized with an infrared spectrometer to perform surface enhanced infrared absorption (SEIRA) spectroscopy with electrochemical control. The multichannel instrument has also been utilized to study mass transport in mesoporous films. Sample data from these ongoing efforts are demonstrated later in this report.

Statement of the Problem Studied

Our group is interested in understanding the interface between the electrode and electrolytes. Knowledge in this area is important because chemical interactions at the electrode/electrolyte interface determine the type, rate, and efficiency of electron transfer processes that control device efficiencies.^{1,2} We have chosen to pursue studies that involve simultaneous infrared (IR) spectroscopy with electrochemical perturbation. We have modeled our work after other researchers that have utilized these techniques with ‘traditional’ electrolytes (e.g., aqueous systems) at metal electrodes.³ However, we have turned our focus to ionic liquid electrolytes which, to date, have been largely unexplored. In the past decade, ionic liquids (ILs) have been targeted as electrolytes for a wide variety of electrochemical applications however, there is presently a knowledge gap with respect to characterizations of the interfaces between electrodes and IL-based systems.³ This report shows our progress towards building capabilities that will allow us to perform systematic studies that provide important dynamic structural information of the interface between ILs and electrode surfaces.

Summary of Important Results

- We have performed simultaneous electrochemical and spectroscopic (SEIRA) experiments that probe the interactions of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIm TFSI) at nanostructured gold electrodes. Research assistants have been trained and are now performing spectroelectrochemical experiments with mixed systems (e.g., EMIm TFSI + acetonitrile).
- Our group has begun to synthesize mesoporous films. We have and will continue to utilize the multichannel potentiostat to characterize transport within these films. (The multiplexing abilities of the potentiostat allow us to perform these characterizations during SEIRA experimentation.)

Simultaneous Electrochemical + SEIRA Experiments

When a potential is applied to an electrode, physics still dictates that charge be compensated between the electrode and solution as:

$$-\sigma_{\text{metal electrode}} = \sigma_{\text{solution}}$$

Equation 1

In the case of pure ionic liquid (IL) solvents, the fact that the solution is composed solely of ions puts unique constraints on the way in which ions can (re)organize to form a potential gradient, **Figure 1**. To date, there remains debate on the exact nature of the (double layer) structure of ILs at charged

surfaces. Additionally, there is evidence that the time scales over which the solution can reorganize to changes in potential are lengthened significantly primarily due to ion-ion interactions, hydrogen bonding, et cetera that increase the viscosity. This raises the possibility of manipulating the structure of ILs by appropriate (fast) waveforms that play kinetic and thermodynamic solution structures off of one another.

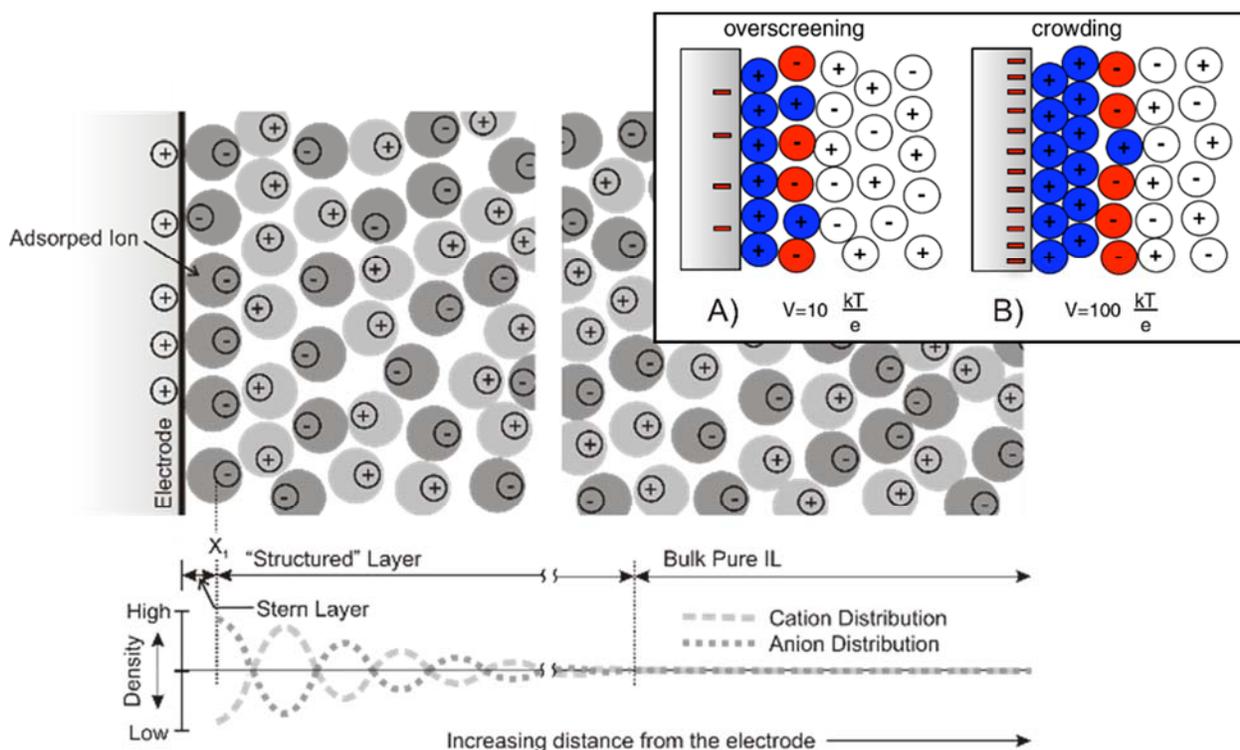


Figure 1: Cartoons illustrating the double layer in for an IL. (Not to scale, nor should shapes of ions be taken literally.) The inset in the upper right corner is from⁴: M. Z. Bazant, B. D. Storey, A. A. Kornyshev, *Phys. Rev. Lett.*, **2011**, *106*, 046102 1-4. Our group is working on experiments that probe the true structure and nature of ILs at metal surfaces.

Figure 2 shows a spectroelectrochemical cell in the standard Kretschmann geometry for performing SEIRA measurements.⁵ Infrared (IR) light is directed through an attenuated total reflectance (ATR) crystal onto which a thin (several nm thick) nanostructured film metal electrode has been deposited. Light penetrates the electrode from the back and excites surface plasmons at the electrode/electrolyte interface. Penetration of the evanescent wave into solution is shallow (<100 nm) compared to traditional ATR (~1-5 μm with no metal film) and is strongly dependent on the types of materials (refractive indices), angle of incidence, the wavelength of light, and the thickness (of the film electrode). In the case of SEIRA, thin 'island-like' films (but still conductive) promote surface plasmon resonance that amplifies the absorbance of adsorbed species in addition to providing a larger interfacial surface area (than a smooth metal film). As IR light excites surface plasmons, the dipole moments (μ) of adsorbed species at the metal surface (at right) interact constructively or destructively depending on the geometry of interaction. Infrared absorptions are thus indicative of the type of adsorbed species as well as the average orientation. With a sufficiently fast and sensitive spectrometer/detector, SEIRA spectroscopy provides insight as to the real-time structural dynamics of

ILs when performed with simultaneous manipulation of the electrode potential (e.g., during cyclic voltammetry).

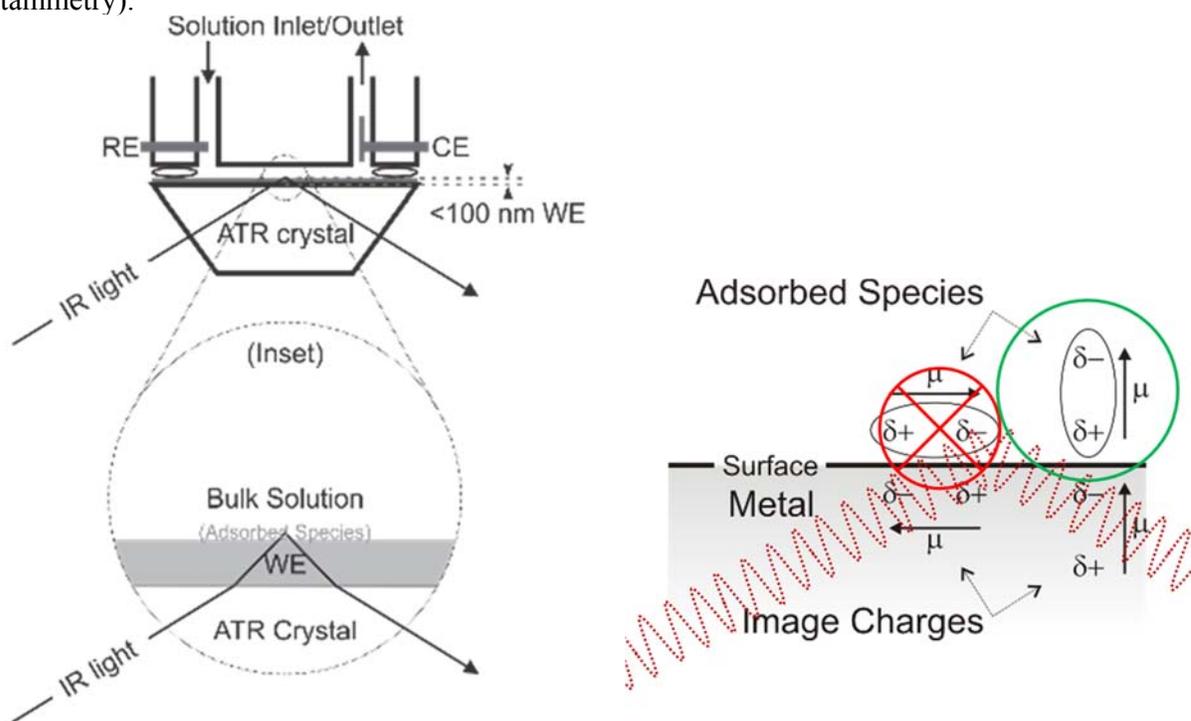


Figure 2: Cartoons illustrating the surface enhanced infrared absorption (SEIRA) spectroscopy via an attenuated total reflectance (ATR) crystal modified with a nanostructured metal film working electrode. The so called, ‘Kretschmann’ ATR geometry (at left) has a thin ($< \sim 100$ nm) metal film which enables simultaneous spectroscopic and electrochemical experiments.⁵

For spectroelectrochemical measurements, we have employed the Kretschmann cell geometry with a standard three electrode system controlled and measured by (one channel of) the BioLogic VMP potentiostat. This instrument has allowed us to collect data such as shown in **Figures 3** and **4**. (Spectral data are offset for clarity.) These data are the difference spectra for cyclic voltammetric experiments. Data detail an evolving, dynamic system as EMIm TFSI moves in response to the voltammetric perturbation. In this experiment, 10 CV experiments were performed in succession. The scan rate was fixed at 70 mV/s. In **Figure 3**, spectral data for the first CV of the series was recorded at +1.2 V and was utilized as the background (subtractive) scan. (This is denoted by the red box in the waveform shown at the upper left of the figure.) Spectral differences for the 5th, 6th, 7th, 8th, 9th, and 10th CVs (at +1.2 V) in the series are produced by subtracting the spectral data collected during the 1st CV. (The relative timing is denoted by the color coordinated boxes in the upper left-hand waveform inset.) The shaded regions denote the approximate position of absorption bands for symmetric (ν_s) and asymmetric (ν_{as}) vibrational modes for the TFSI anion: $1055\text{ cm}^{-1} - \nu_{as}(\text{SNS})$, $1134\text{ cm}^{-1} - \nu_s(\text{SO}_2)$, $1221\text{ cm}^{-1} - \nu_{as}(\text{CF}_3)$, $1238\text{ cm}^{-1} - \nu_s(\text{CF}_3)$, $1327\text{ cm}^{-1} - \nu_{as}(\text{SO}_2)$, and $1357\text{ cm}^{-1} - \nu_{as}(\text{SO}_2)$.¹⁰ The data show an increase in the concentration of anion at the surface as the system evolves.

Data demonstrated in **Figure 3** are reasonable since the electrode is poised positive while data was collected (at these particular points) and therefore attracts anions. However, it is interesting to note (counterintuitive) that **Figure 4**, which is recorded while the working electrode is poised at -2.0 V also shows a system that evolves to move more anions near the electrode surface. Relative to the first CV,

cycles 2 and 3 show less overall anion concentration in the difference spectra. The 4th cycle is relatively flat and implies the amount of anion is roughly similar to the first cycle. From the 5th cycle onward, the difference spectra indicate more anion is building up at an electrode surface (relative to the starting concentration) while poised to a strongly negative potential. This somewhat pyridoxal result is mostly likely explained by the combination of the scan rate (time scale of the experiment) with the viscosity of the IL system interrogated. In other words, structural hysteresis that involves a system of associated cations and anions that cannot move in time with the imposed waveform. We believe this to be an interesting result, however, because it suggests that the right combination of waveform (shape and timescale) with electrolyte system may allow the creation of ‘kinetic’ structures not otherwise observed under ‘thermodynamic’ (e.g., slow experimental) conditions.

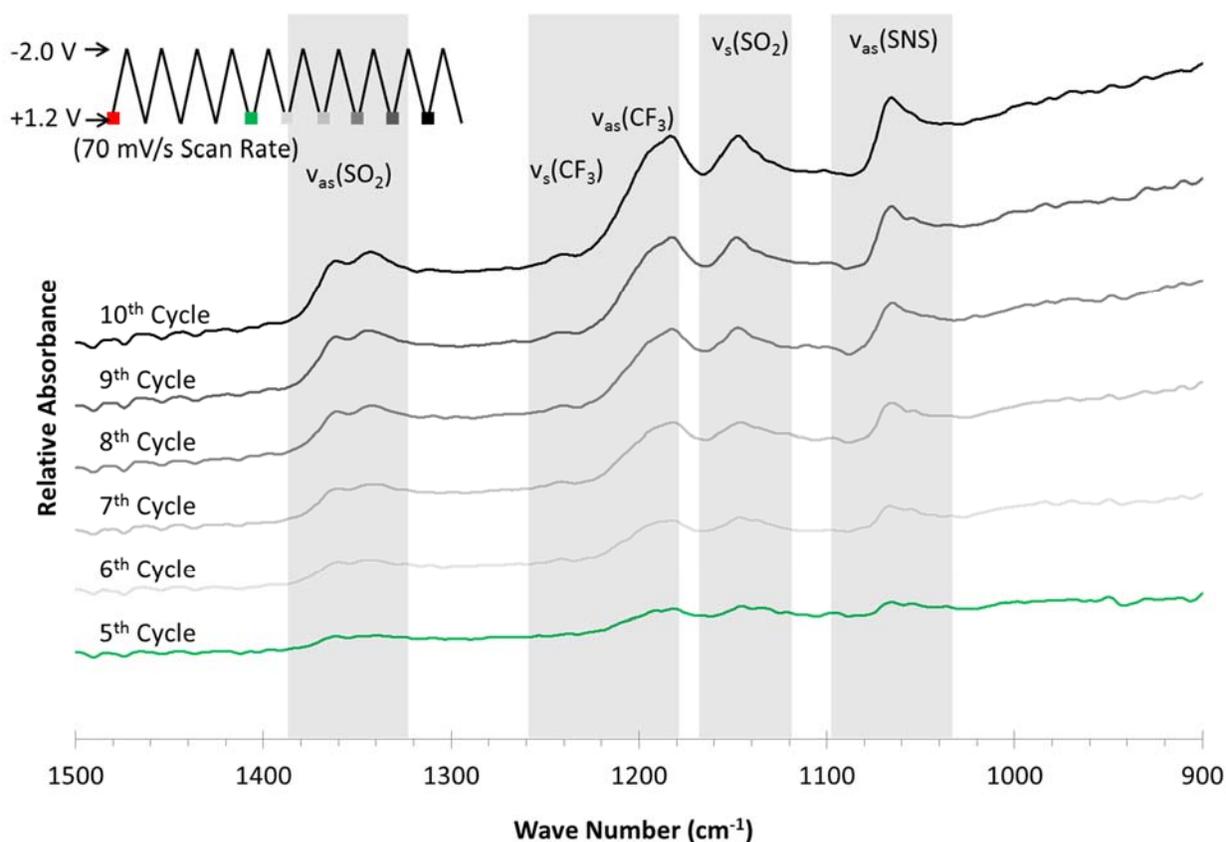


Figure 3: Data are the SEIRA absorbance difference spectra for EMIm TFSI at a 4.9 nm thick gold film electrode on a Ge ATR crystal during cyclic voltammetry (CV, scan rate = 70 mV/sec). Spectra are stacked on a relative scale for viewing purposes. Spectra for potential = +1.2 V during the 5th to 10th cycle, respectively, have been background subtracted utilizing the spectra taken during the first cycle (■). Data indicate hysteresis in that the anion concentration at the electrode appears to increase as cycles are repeated. This is consistent with literature data but also suggests that ‘kinetic’ structure might be controllably ‘built’ into the double layer by an appropriate waveform (time scale).

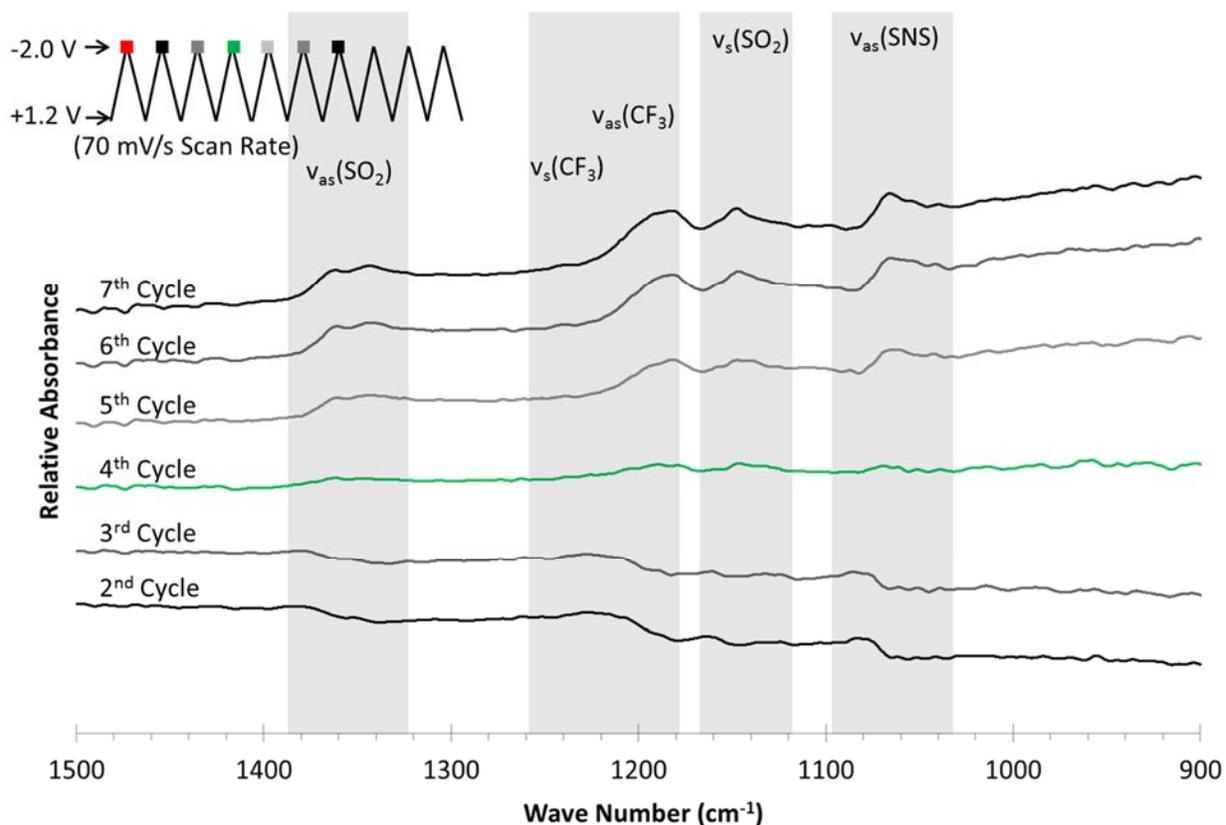


Figure 4: Data are the SEIRA absorbance difference spectra for EMIm TFSI at a 4.9 nm thick gold film electrode on a Ge ATR crystal during cyclic voltammetry (scan rate = 70 mV/sec). Spectra are stacked on a relative scale for viewing purposes. Spectra for potential = -2.0 V during the 2nd to 7th cycle, respectively, have been background subtracted utilizing the spectra taken during the first cycle (■). Data again indicate hysteresis in that the anion concentration at the electrode appears to increase as cycles are repeated. It is interesting to note that while cycles 2 and 3 show less anion near the electrode, cycles 4 to 7 display more anion character. Going forward, we are working to more directly comparing results for CV experiments with potential step-type experiments to determine what absolute structural differences ('kinetic' versus 'thermodynamic') may in fact exist.

As we move forward, we are trying to quantitatively assess the dynamics of IL-based systems. In particular, we hope to relate the observed dynamic behavior to the viscosity of the electrolyte solution. To this end and to make analyses more clean and simple, we will move from CV to potential step experiments in attempt to capture double layer rearrangement as a function of time.

Characterizations of Mesoporous Film Electrodes

Simultaneous to SEIRA experimentation, we are working on new electrode materials for study by utilizing as working electrode coatings on ATR crystals (as alternatives to Au). In addition, the development of novel thin film mesoporous electrodes may have use in applications ranging from sensors to solar cells. We are utilizing the Biologic Instrument to characterize these materials. For example, we have also fabricated TiO₂ and ZnO semiconducting mesoporous thin film electrodes with and without graphene dopants.⁶ To date, all films have been produced using the sol-gel method. The general procedure has been to add Ti/Zn nanoparticles to ethanol and Triton X-100 with sonication

and stirring for about 30 min. Next, ~0.5g of α -terpineol was added with sonication and stirring for an additional 30 min. Separately, ~0.10 g of ethyl cellulose was added to ~0.9 g ethanol with stirring. Both mixtures were combined with sonication and stirring for one hour. At this point in the procedure, graphene (produced utilizing the procedure previously mentioned) was often added. Films were cast via the doctor blade technique and then sintered in an oven at 450 °C for 45 min. The overall process is shown pictorially in **Figure 5**.

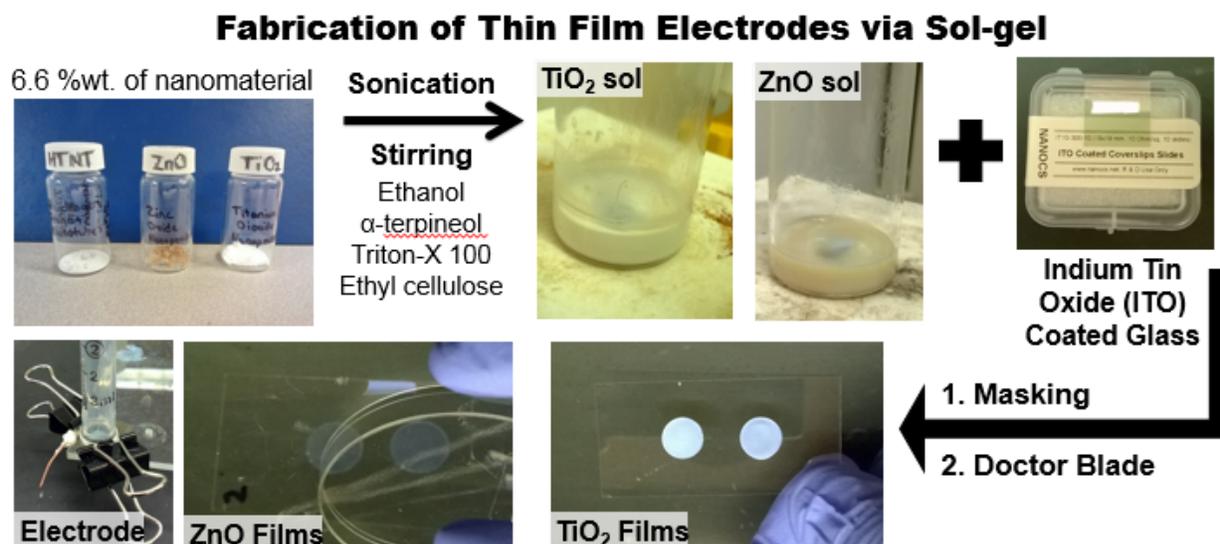


Figure 5: Pictures of the production of thin mesoporous films. We are utilizing these systems as model systems to study transport of electrolyte and electroactive species.

Table 1 below presents preliminary transport data for TiO₂ and HTNT mesoporous films. The diffusion coefficients for methylene blue chloride (1 mM in 5% wt. Na₂CO₃, pH=10.4) within films cast onto indium tin oxide (ITO) coated glass slides are measured by cyclic voltammetry (reference electrode: 4M Ag/AgCl, counter electrode: Pt wire) and calculated according to¹:

$$i_p = (2.69 \times 10^5) n^{3/2} A D_o^{1/2} C_o^* v^{1/2}$$

Equation 2

Table 1: Diffusion coefficients calculated by CV experiments for a bare ITO working electrode as well as TiO₂ and HTNT mesoporous films. Data collected with the new Biologic VMP instrument.

Working Electrode/Film	$A(D_o)^{1/2}$ (cm ³ /s ^{1/2}) x 10 ⁻⁴	D_o (cm ² /s) x 10 ⁻⁷	Std Dev (cm ² /s) x 10 ⁻⁷
ITO	4.56	5.764	0.002
ITO/TiO ₂	3.78	3.9650	0.0003
ITO/HTNT	3.42	3.2326	0.0008

Summary and Ongoing/Future Work

A Biologic VMP 16 Channel Potentiostat has been procured and is greatly enhancing our electrochemistry program at Bradley University.

Going forward, we will continue to utilize work to maximize utilization of the Biologic VMP instrument. In particular, the use of sixteen independent channels will help to forward multiple projects simultaneously, for example:

- 1) We continue to collect SEIRA data for pure ILs and IL-based systems.
- 2) We will continue to characterize new electroactive materials and new electrode designs.

Bibliography

1. A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications, 2nd ed.*, **2002**, John Wiley & Sons, Inc., New York, NY.
2. M. Yoshida, A. Yamakata, K. Takanabe, J. Kubota, M. Osawa, K. Domen, *J. Am. Chem. Soc.*, **2009**, *131*, 13218-13219.
3. A. Kokorin (Ed.), *Ionic Liquids: Applications and Perspectives*, **2011**, InTech, New York, NY.
4. M. Z. Bazant, B. D. Storey, A. A. Kornyshev, *Phys. Rev. Lett.*, **2011**, *106*, 046102 1-4.
5. E. Kretschmann, *Z. Physik*, **1971**, *241*, 313-324.
6. Y. Tang, *et al.*, *Adv. Mater.*, **2004**, *26*, 6111-6118.