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14. ABSTRACT

This report describes a project focused on characterization of IL-based electrolyte/electrode systems via simultaneous electrochemical and spectroscopic experiments. The types of data we are generating are crucial to the understanding the microscopic (molecular and ionic) dynamics of electrolyte/electrode interfaces, information that is a prerequisite to engineered progress of many important energy conversion processes and devices (e.g., supercapacitors). In specific, surface enhanced infrared absorption (SEIRA) spectroscopy data of pure ionic liquid

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FINAL PROGRESS REPORT

“Characterizing Microstructures at Ionic Liquid/Electrodes Interfaces”

Proposal #: 64558-CH-YIP
Agreement #: W911NF-13-1-0448
Final Report

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Abstract

This report describes a project focused on characterization of IL-based electrolyte/electrode systems via simultaneous electrochemical and spectroscopic experiments. The types of data we are generating are crucial to the understanding the microscopic (molecular and ionic) dynamics of electrolyte/electrode interfaces, information that is a prerequisite to engineered progress of many important energy conversion processes and devices (e.g., supercapacitors). In specific, surface enhanced infrared absorption (SEIRA) spectroscopy data of pure ionic liquid (IL) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm TFSI) as well as EMIm TFSI cut with molecular additives (i.e., acetonitrile and water) at nanostructured gold film electrodes are discussed. Results have demonstrated dynamic structural changes in the double layer for neat IL systems (i.e., EMIm TFSI) as well as mixed EMIm TFSI/acetonitrile at gold. Moreover, the time dependence of dynamics as a function of composition (and related solution viscosity) for mixed systems is discussed.

Statement of the Problem Studied

The interface between the electrode and electrolyte determines the type, rate, and efficiency of electron transfer processes that control device efficiencies.[1,2] In the past few decades, studies that have combined simultaneous infrared (IR) spectroscopy with electrochemical perturbation have produced important data that characterize interfaces between 'traditional' electrolytes and various types of electrode surfaces; and, this information has resulted in improved devices and processes.[3] 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] In this report, progress towards systematic studies that provide dynamic structural information of the interface between ILs and electrodes are discussed. This type of data is essential to analytically cope with the wide ranging tunable nature of ILs for a variety of applications. Simply put, rational design of many electrochemical processes that employ ILs pivot from these types of seminal studies.

Summary of Important Results

- Performed potential step and cyclic voltammetric experiments that probe the response of EMIm TFSI under potentiometric perturbation. A first publication on this work has been accepted and is in press. At least one additional publication is being developed.
- We studied several model systems including EMIm TFSI, in part, because of a recent study: "Hysteresis of Potential-Dependent Changes in Ion Density and Structure of an Ionic Liquid on a Gold Electrode: In Situ Observation by Surface-Enhanced Infrared Absorption Spectroscopy" by Motobayashi and co-workers.[4] EMIm TFSI is of interest due to its wide electrochemical potential window (stability) and has been utilized, for example, in the construction of supercapacitors. We have characterized systems and conditions not previously discussed in literature data/reports.
- Our group has designed and implemented several new cell designs that enables ongoing experiments with 'traditional' an FTIR spectrometer as well as a laser-based imaging system.
- Our group has synthesized graphene as well as other electrode materials for ongoing SEIRA experimentation. We have utilized these materials in the production of mesoporous films and have begun to characterize transport properties therein.

- Nine unique undergraduate research assistants have been trained to perform spectroelectrochemical experiments. Eight have graduated and are continuing on in STEM-related careers. (One remaining student is on track to graduate in 2019 with a BS in chemistry.)

Summary of Student Engagement

During this project, 9 undergraduates and 1 graduate student (David Gray, was both a BS and MS graduate of Bradley University) have engaged in research and 8 of these students have graduated with STEM degrees. Of 8 graduates at least 5 have continued or are planning to continue with some form of advanced degree. One student, Carl Meunier, has gone on to receive a highly competitive NSF graduate fellowship award at NC State University.

- Bryce Egan (BS, currently in PhD program at U of Miami, OH)
- Daniel Parr (BS, currently in PhD program at U of Iowa, IA)
- Christina Zibart (BS, currently teaching high school science/chemistry)
- Carl Meunier (BS, currently NSF Fellowship Awardee in PhD program at NC State U, NC)
- Kasim Malik (BS, accepted to medical school)
- Jacob Chrestenson (BS, planning on medical school)
- Michael Molter (BS, working towards an additional engineering degree)
- David Gray (BS + MS, currently employed as a chemist)
- Hailemariam Mitiku (plans to graduate with BS in 2019)

During this project, 12 presentations which included student co-authors were given. This included 5 oral presentations and 7 poster presentations and regional, national, and international venues.

Description of SEIRA Experimental Findings

Figure 1: Instrument and cell setup used for SEIRA measurements.

Figure 1 details the standard spectroelectrochemical setup. Then (~ 10 nm) thick gold working electrode (WE) is sputter coated on to an attenuated total reflectance (ATR) crystal. The ATR crystal placed in a standard Fourier Transform IR (FTIR) spectroscopy (optical) setup. The coated crystal is placed with the WE facing up and covered with a sealed Teflon electrochemical cell. The cell has a small cylindrical opening to hold around 1 mL of IL-based electrolyte solution as well as a sealed port to accept the counter/reference electrode. With this set up, IR light is able to generate surface plasmons at the electrode surface enables the SEIRA effect detailed in **Figure 2**.

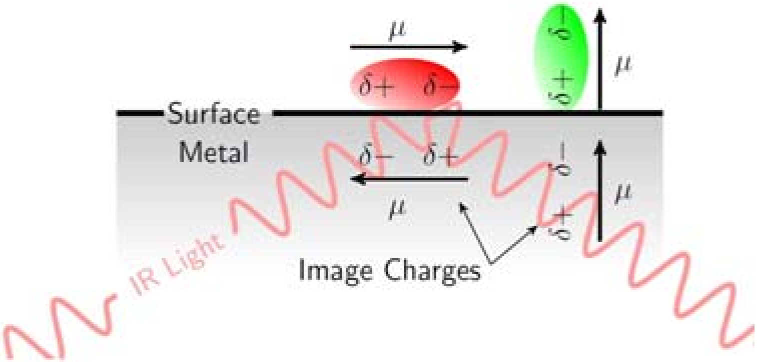

Figure 2: Examples of geometries of dipole moments of the species at a metal surface (i.e., the WE). Dipole moments parallel to the metal surface result in destructive interference while dipole moments perpendicular to the metal surface result in constructive interference.

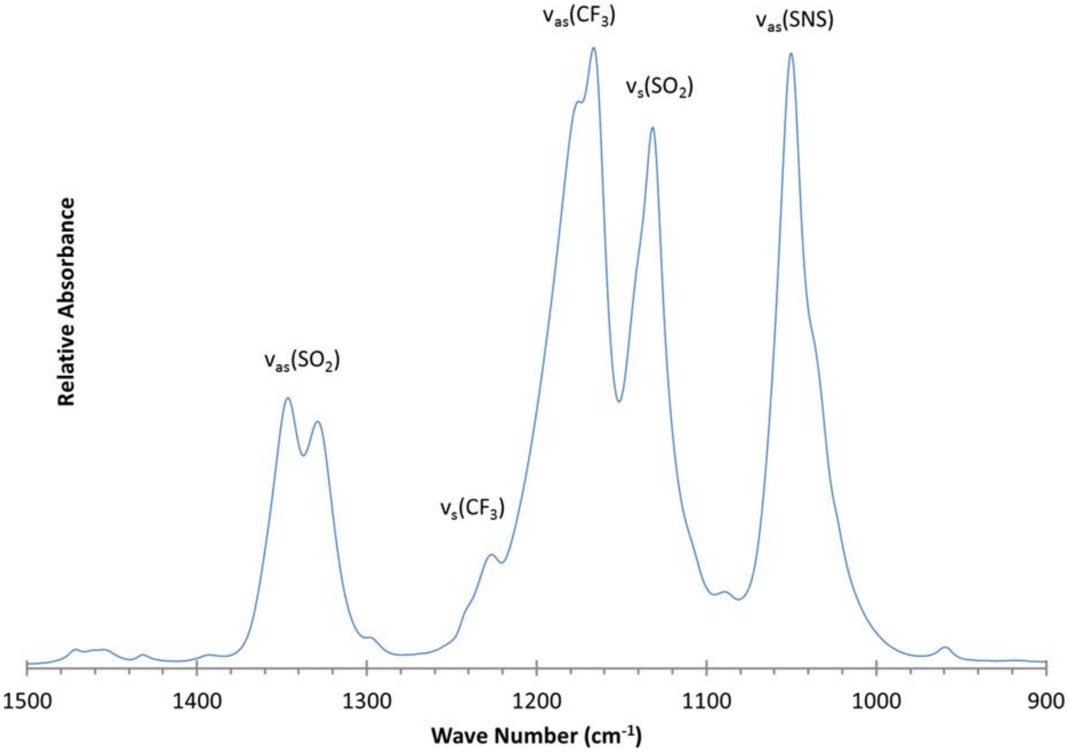

Figure 3: Absorbance spectrum of EMIm TFSI.

An example IR absorbance spectrum is shown in **Figure 3**. **Figure 4** shows how absorbance changes for a EMIm TFSI electrolyte as a function of different potentials applied across the WE and counter/reference electrode setup of the spectroelectrochemical cell. A spectrum was collected with the potential held at 0.0 V. (The potential was held at 0.0 V for about 30 minutes prior to collecting the spectrum.) After 5 minutes, another spectrum was collected with the potential still held at 0.0 V. Additional spectra were collected after holding the potential at -0.5, -0.7, -1.0, -1.5, -2.0, and -2.5 V, respectively. Each spectra was collected after allowing the system to equilibrate for 5 minutes at the new potential. **Figure 4** shows the difference (by subtraction) of the spectra. For each potential, the spectra collected after 5 minutes of equilibration time is compared to the spectra recorded at the beginning of the experiment at 0.0 V. 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 cm^{-1} – ν_{as}(SNS), 1134 cm^{-1} – ν_s(SO_2), 1221 cm^{-1} – ν_{as}(CF_3), 1238 cm^{-1} – ν_s(CF_3), 1327 cm^{-1} – ν_{as}(SO_2), and 1357 cm^{-1} – ν_{as}(SO_2).[4] (It may also be helpful to refer back to **Figure 3** as spectral differences relate to the absorbance bands detailed in that figure.) As expected, the difference spectrum is flat for the '0.0 V'. Absorbances become more pronounced as the WE moves to more negative potentials (relative to the counter/reference electrode). 'Negative' peaks appear because anions are, apparently, moving away from the surface as the electrode is polarized to increasingly negative potential.

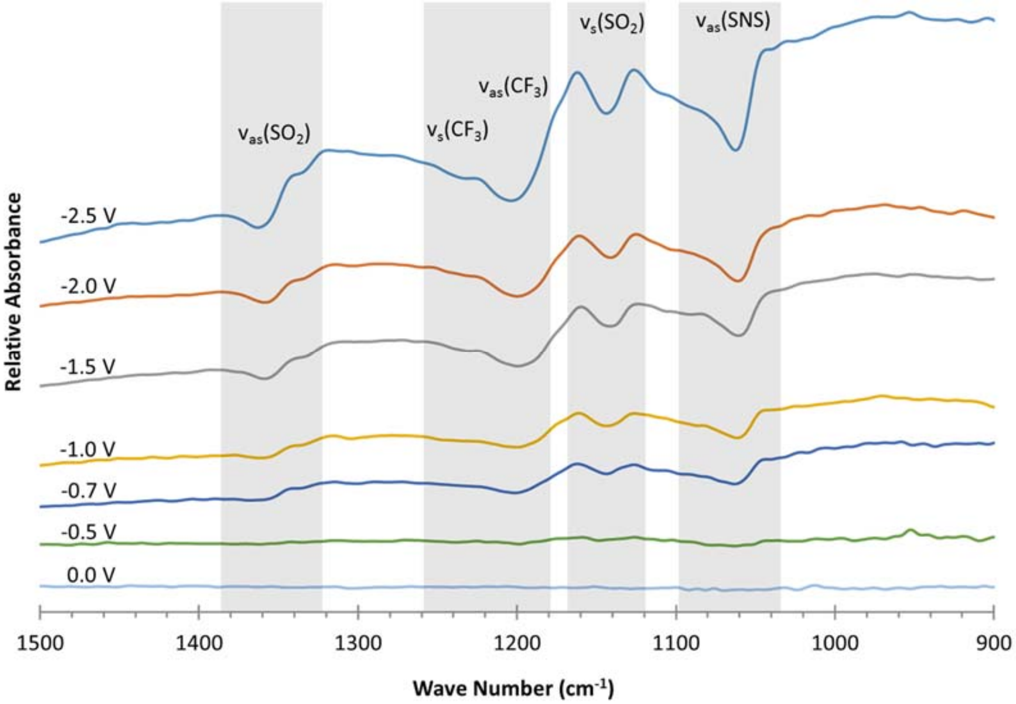

Figure 4: Surface-enhanced infrared spectra of EMIm TFSI at the surface of a gold electrode at varying potentials. Absorbances associated with the TFSI anion are highlighted, and can be seen to decrease as the gold electrode has more negative charge.

The results shown in **Figure 4** were obtained very early in the life of this project. These are 'expected' and are in agreement with standard theory and similar to results published by Motobayashi and co-workers.[4] This type of experiments were a means to train undergraduate researchers and were a sort of 'sanity check' that our group utilized to make sure our setup and protocols were sound.

Results described in the rest of this report are surprising new findings that are still not fully understood. Although this project is 'officially' concluded, work is ongoing to try to understand and quantify some of the surprising observations made by our group.

Figures 5 and **6** show difference spectra for CV experiments and detail an evolving, dynamic system (EMIm TFSI). Spectral data are offset for clarity. In this experiment, 10 CV experiments at 70 mV/s scan rate were performed in succession. In **Figure 5**, 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 cm^{-1} – ν_{as}(SNS), 1134 cm^{-1} – ν_s(SO_2), 1221 cm^{-1} – ν_{as}(CF_3), 1238 cm^{-1} – ν_s(CF_3), 1327 cm^{-1} – ν_{as}(SO_2), and 1357 cm^{-1} – ν_{as}(SO_2).[4] The data show an increase in the concentration of anion at the surface as the system evolves.

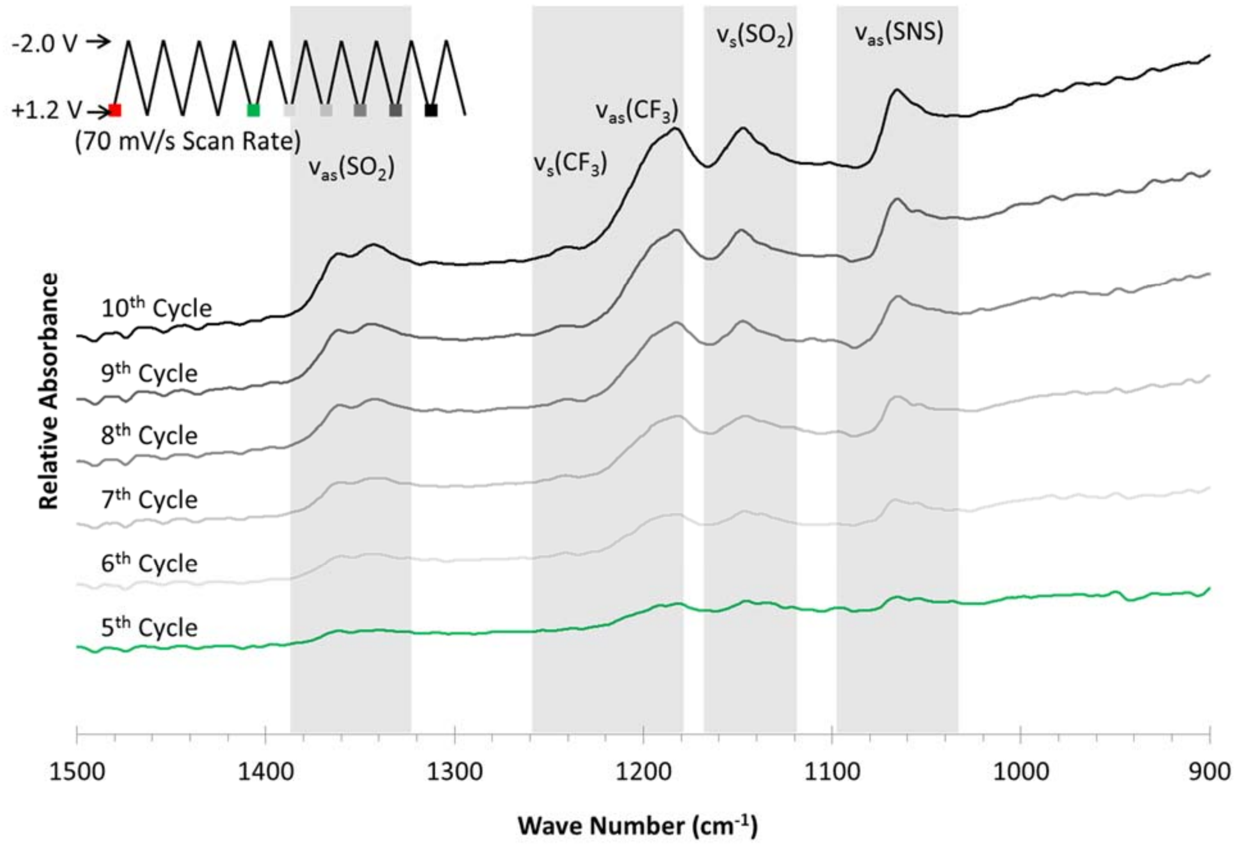

Figure 5: Data are the SEIRA difference spectra for EMIm TFSI at a 4.9 nm thick gold film electrode on a Ge ATR crystal during cyclic voltammetry (CV, scan rate = 70 mV/sec). Spectra are stacked on a relative scale for viewing purposes. Spectra for potential = +1.2 V during the 5th to 10th cycle, respectively, 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).

Data demonstrated in **Figure 5** are likely not surprising since the electrode is poised positive while data was collected (at these particular points) and therefore attracts anions. However, it is interesting to note that **Figure 6**, 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.

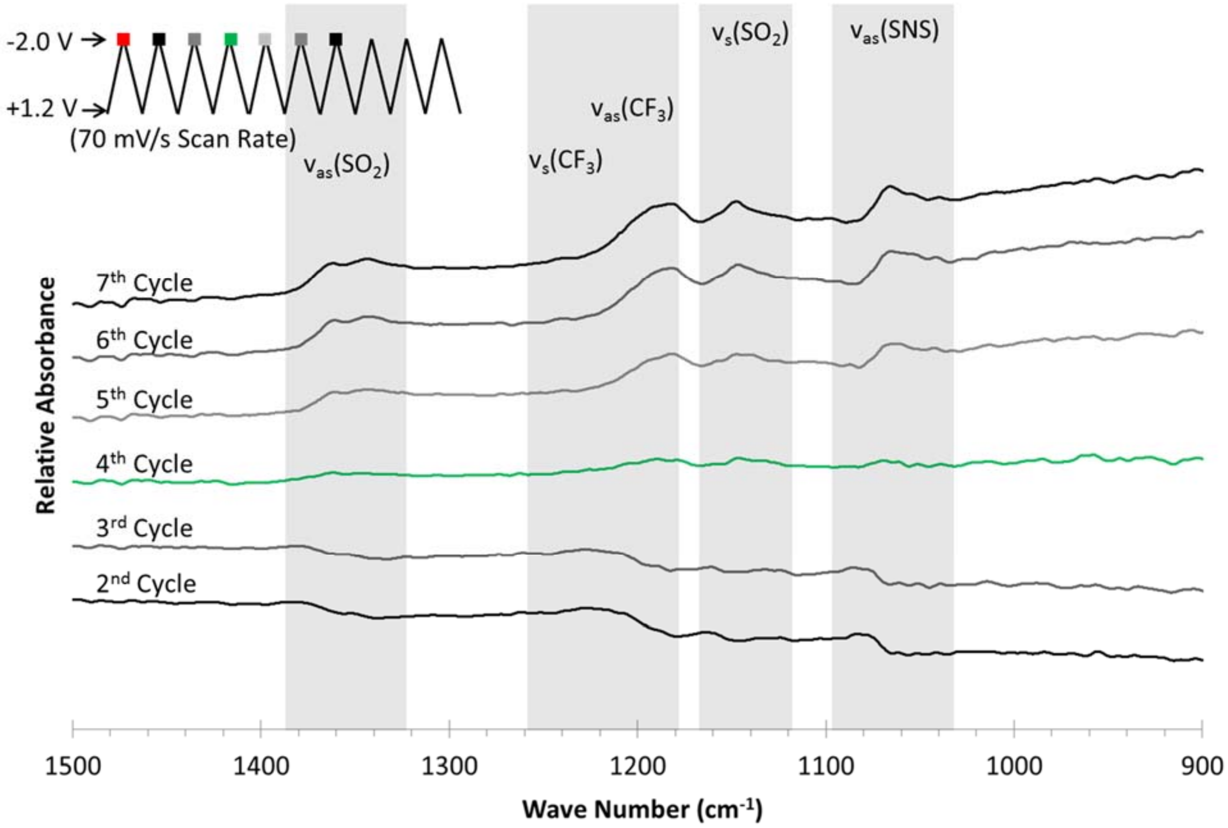

Figure 6: Data are the SEIRA absorbance difference spectra for EMIm TFSI at a 4.9 nm thick gold film electrode on a Ge ATR crystal during cyclic voltammetry (scan rate = 70 mV/sec). Spectra are stacked on a relative scale for viewing purposes. Spectra for potential = -2.0 V during the 2nd to 7th cycle, 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.

During the course of the project, our group tried, with varying degrees of success, to reproduce results like those shown in **Figures 5** and **6**. In short, various scan rates of CV were employed. Whereas results were often *qualitatively* similar, we have yet to reproducibly obtain results that are *quantitatively* understandable. Whereas CV experiments inherently lead to complex dynamics, we decided to utilize potential step experiments in attempt to simplify data analyses. In particular, we aimed to relate the observed dynamic behavior to physical parameters such as viscosity of the electrolyte solution. **Figures 7** and **8** are examples of spectroscopic data that captures double layer rearrangement as a function of time (after a potential step). **Figure 7** shows raw data for neat EMIm TFSI as the Au electrode is switched from 0.0 V to -1.5 V. (The working electrode was equilibrated at 0.0 V for 30 minutes prior to performing the potential step.) **Figure 8** shows raw data for a similar experiment utilizing a mixture of EMIm TFSI with ACN (1 mol to 1 mol ratio) at Au. Initial results are that we have observed it takes several minutes for the system to fully adjust after the potential step. In particular, progressive change is observed for the spectral regions associated with $\nu_s(SO_2)$, $\nu_{as}(CF_3)$, $\nu_s(CF_3)$. At first glance, this appears to be in agreement with a recent study by K. Motobayashi and co-workers wherein hysteresis at 2 mV/s scan rate was reported.[4] That said, the results are somewhat surprising in that the 1 mol to 1 mol ratio solution also appears to be quite sluggish. (Motobayashi and co-workers did not explore mixed systems.)

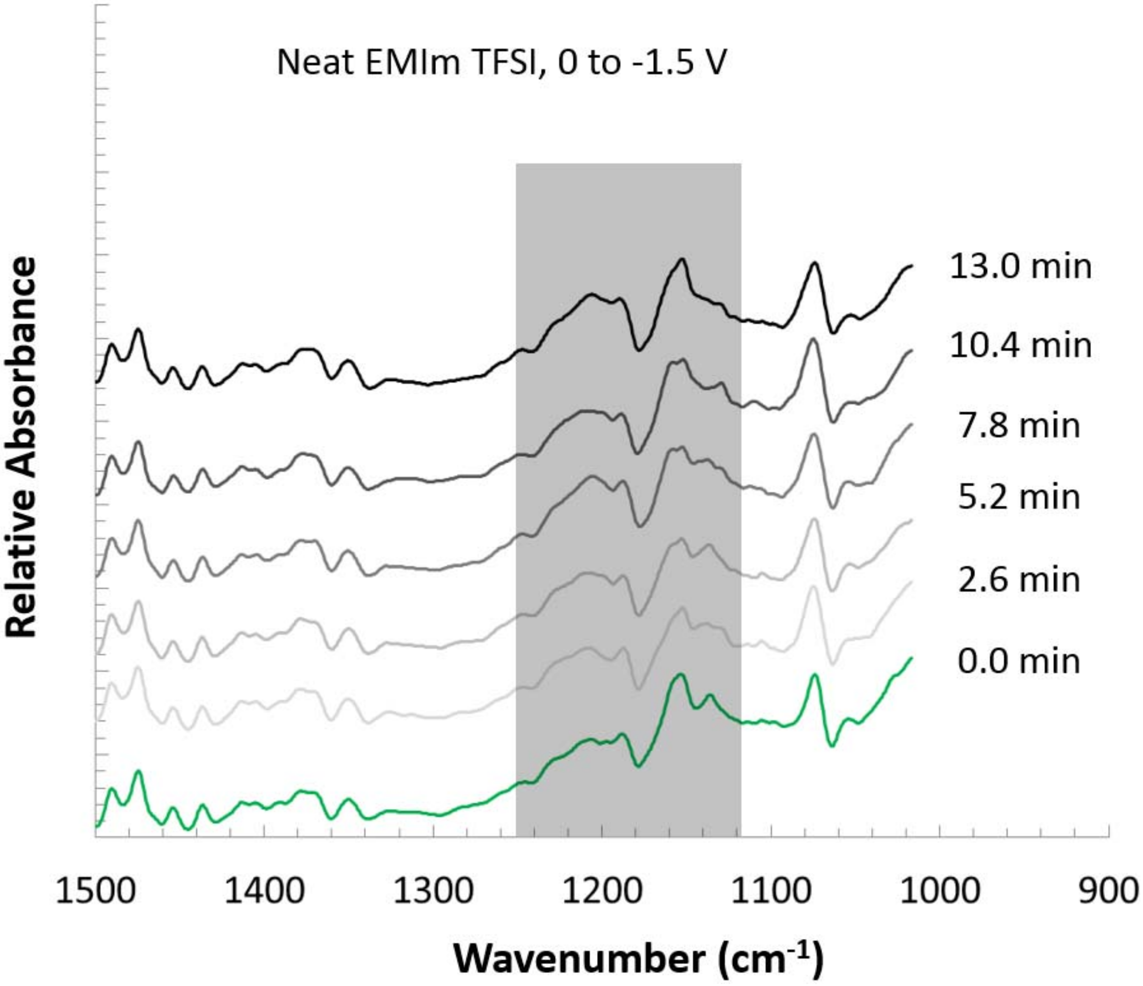

Figure 7: Data are the SEIRA absorbance spectra for pure EMIm TFSI at a 4.7 nm thick gold film electrode on a Si ATR crystal. Data are offset for clarity. Progressive change is observed for the spectral regions (shaded) associated with $\nu_s(SO_2)$, $\nu_{as}(CF_3)$, and $\nu_s(CF_3)$ vibrational modes.

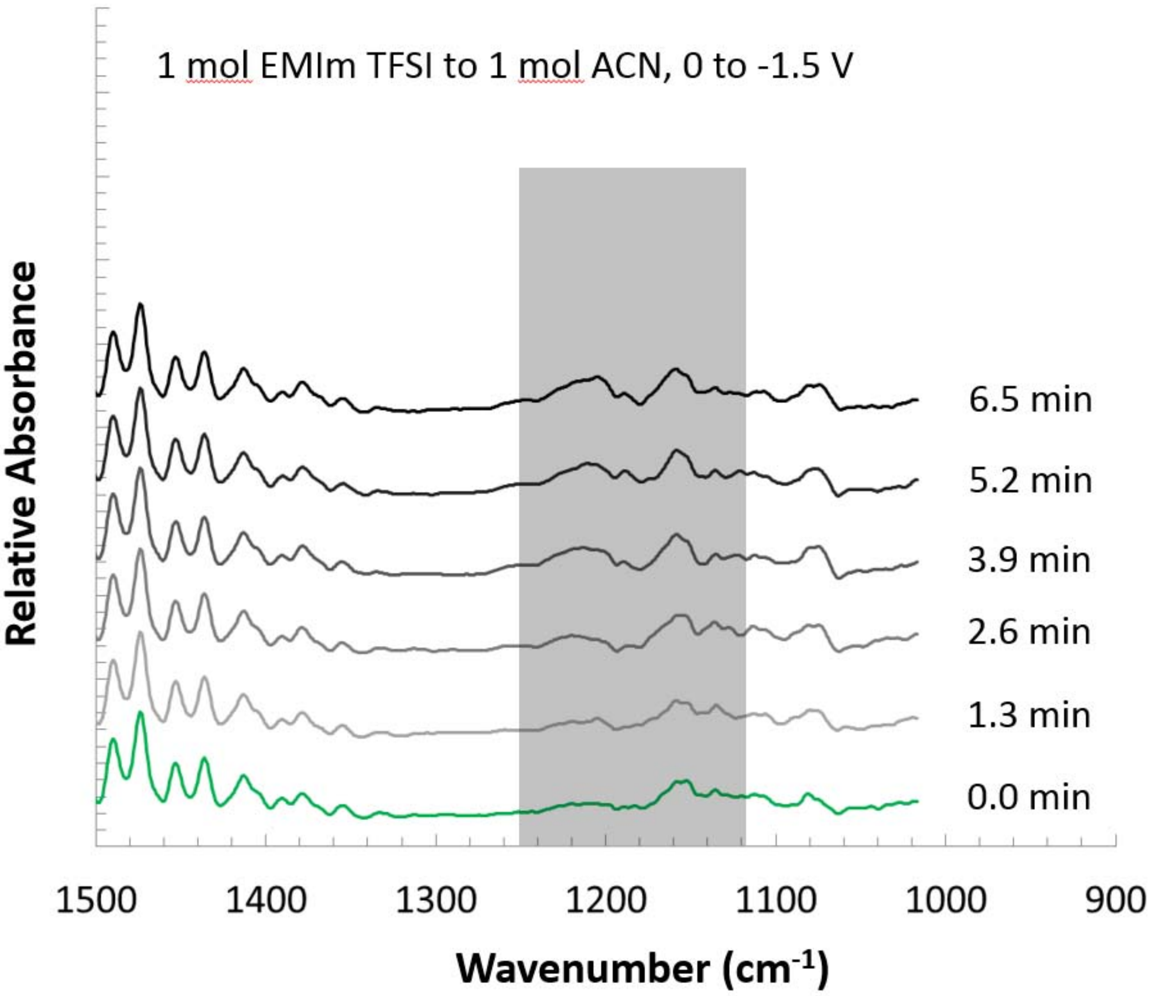

Figure 8: Data are the SEIRA absorbance spectra for a solution that is 1 mol EMIm TFSI mixed with 1 mol ACN at a 4.7 nm thick gold film electrode on a Si ATR crystal. Data are offset for clarity. Progressive change is observed for the spectral regions (shaded) associated with $\nu_s(SO_2)$, $\nu_{as}(CF_3)$, and $\nu_s(CF_3)$ vibrational modes. Note that he time frame is for this figure is shorter than for neat EMIm TFSI shown in **Figure 7**.

While potential step experiments have given more insight, quantitative results that are reproducible remain elusive. There does appear to be correlations with viscosity (i.e., faster dynamics in systems with lower viscosity) however, more study is underway to perfect the results. It is apparent that solvent purity (i.e., adventitious water content and other impurities that may be introduced during the synthesis of ILs) plays an important role in reproducibility. There is indication that if the purity/composition of IL systems is precisely tuned, that interesting ion dynamics can be coordinated by control of the shape and time domain of electrochemical perturbations. In particular, electrochemical syntheses and catalysis may have one day be applications that benefit from this fundamental understanding.

Description of Other Electrochemical Experimental Findings

Simultaneous to SEIRA experimentation, our group has worked to develop new electrode materials for study (as working electrode coatings on ATR crystals. Moreover, we have branched out to characterize novel thin film mesoporous electrodes which may have use in applications ranging from sensors to solar cells.

The synthesis, functionalization, and characterization of high quality monolayer graphene is of interest as an electrode material in electrochemical devices. We have adapted several methods of graphene synthesis found in literature for our purposes.[5] For example, graphene from graphite that is oxidized using concentrated sulfuric acid and potassium permanganate. Sodium borohydride is then added to graphite oxide suspended in nanopure (>18MΩ resistivity) water by ultrasonication. The mixture was washed and filtered before adding concentrated sulfuric acid and allowed to react for twelve hours before, a final filtering and washing procedure. The final product is a suspension of graphene that was cast into thin films and is being utilized in ongoing SEIRA experiments.

Our group has also successfully fabricated TiO_2 and ZnO semiconducting mesopourous 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 9**. Selected scanning electron microscopy of selected materials we are studying are shown in **Figure 10**.

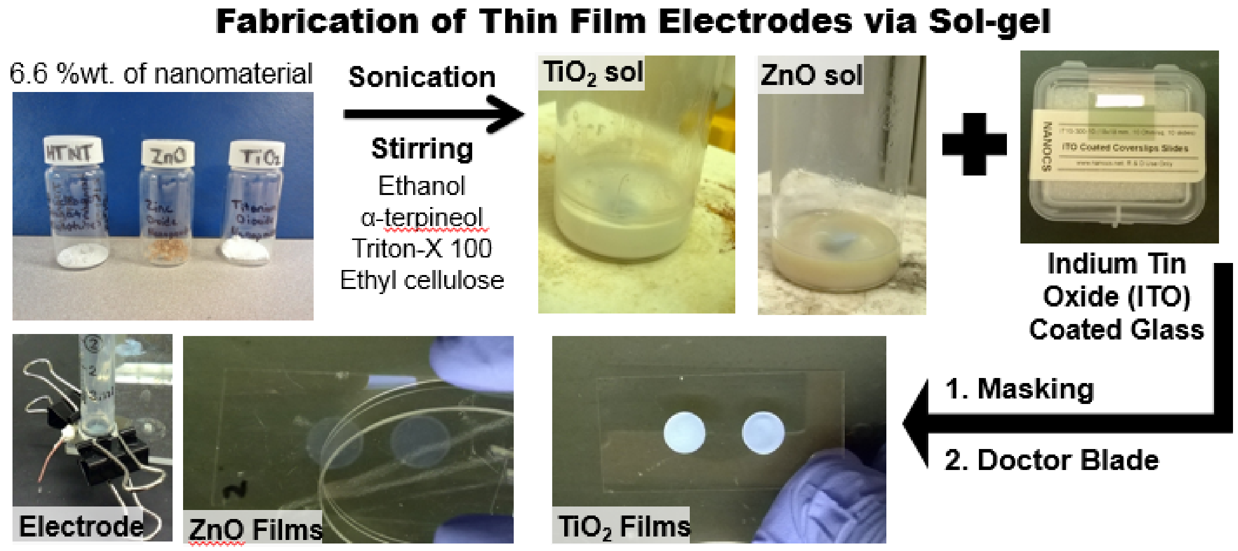

Figure 9: Pictures of the production of thin mesoporous films. We are utilizing these systems as model systems to study transport of electrolyte and electroactive species.

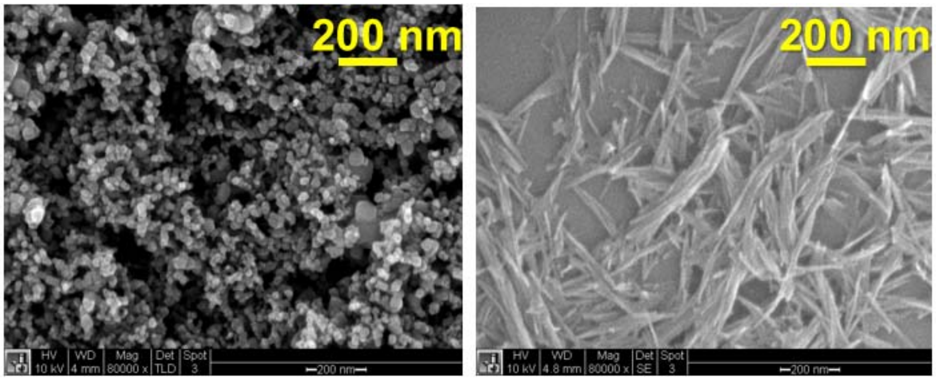

Figure 10: Shown are SEM imaging data of a sample titanium nanoparticle film as well as hydrogen titanate nanotubes (HTNTs) we intend to study during the next performance period.

Table 1 below presents preliminary transport data for TiO_2 and HTNT mesoporous films. The diffusion coefficients for methylene blue chloride (1 mM in 5% wt. Na_2CO_3, 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 to:

$$i_p = (2.69x10^5)n^{3/2}AD_o^{1/2}C_o^*v^{1/2}$$

Equation 1

Table 1: Diffusion coefficients calculated by CV experiments for a bare ITO working electrode as well as TiO_2 and HTNT mesoporous films.

Working Electrode/Film	$A(D_o)^{1/2}$ $(cm^3/s^{1/2})$ x10^{-4}	D_o (cm^2/s) x10^{-7}	Std Dev (cm^2/s) x10^{-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 Conclusions

SEIRA has been utilized to interrogate and characterize interesting ion dynamics at thin film conductive electrodes. It is apparent that ‘kinetic’ versus ‘thermodynamic’ control of the structure of species near the electrode surface can be manipulated by appropriate control of electrolyte composition and the shape and timescale and shape of apposite waveforms. Experiments to quantify and pinpoint the key parameters that determine absolute reproducibility are ongoing. It is possible that the surprisingly long time frame for ‘structure’ to persist within IL-based solutions may also play an important role.

Acknowledgements

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