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Major Goals: The major goal for this project was to develop instrumentation for advanced infrared spectroscopy experiments and techniques that characterize electrochemical interfaces in applied systems. In particular, this allows our group to probe and better understand microstructure of ionic liquid (IL) electrolyte solutions near electrode surfaces. Integration of a quantum cascade laser-based spectrometer for surface enhanced infrared absorption (SEIRA) spectrometery enables the characterization of the structure and dynamics of the electric double layer (EDL) in unique ways. Our group is particularly interested in IL systems which exhibit hysteresis at interfaces during, for example, cyclic voltametry. That is, systems for which interfacial structure is dependent on past events (such as previous voltametric experiments). The instrumentation described in this report is designed specifically to be able to perform comparative studies within a single electrochemical cell setup to monitor hysteresis in ILs systems.

Accomplishments: A quantum cascade laser-based spectrometer has been designed, procured, and assembled. The instrument is extremely flexible and enables a wide variety of experiments to be accomplished. A full report has been uploaded.

Training Opportunities: Six students have participated in the design and assembly of the instrumentation and/or have utilized instrumentation for projects. One graduate (Masters) student has graduated and has written a chapter of his thesis detainling spectroscopic studies of electrochemical systems.
Of course, mentorship of students is a strong outcome of these types of projects. Five of six students who have participated in some way on this project have graduated with STEM degrees. The sixth student is on track to graduate with a STEM degree. Each graduate (4 undergraduates and one Masters graduate) has either moved on to additional education in a STEM-related field (e.g., advance degrees in medical fields and/or PhD programs) or is pursuing a professional career in a STEM-related field.

Results Dissemination: Publications have been uploaded and attached to this report. In addition to publicaitons, four poster presentations have been given by students at either regional or national meetings as well as several oral presentations at local events (e.g., weekly seminars at Bradley University).

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

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Participant Type: Faculty
Participant: Aleksander Malinowski
Person Months Worked: 3.00 **Funding Support:**
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DURIP FINAL REPORT

"Quantum Cascade Laser for Characterizing Microstructures at Ionic Liquid/Electrode Interfaces"

Agreement #: W911NF-15-1-0324

Prepared by: Dr. Luke Haverhals
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Abstract

Understanding the interface between ionic liquids (ILs) and electroactive surfaces is of great importance for a wide range of applications including batteries, capacitors, and sensors. This award has enabled the design and build of an infrared (IR) laser-based hyperspectral system capable of making interfacial measurements in electrochemical cells. Characterization of the structure and dynamics of the electric double layer (EDL) by surface-enhanced infrared absorption spectroscopy (SEIRA) is a primary point of interest that the hyperspectral system will enable our group to continue to pursue. Our group is particularly interested in IL systems which exhibit hysteresis at interfaces. That is, systems for which interfacial structure is dependent on past events. The instrumentation described herein is designed specifically to be able to perform comparative studies in a single electrochemical cell setup to monitor hysteresis in ILs systems. This final report describes the successful build of instrumentation and the type of ongoing experimentation it enables.

Statement of the Problem Studied

The development of efficient energy conversion electrochemical processes/devices is critical to maintaining the preeminence of United States military forces and, in particular, the US Army. The technological landscape for tailoring and harnessing ILs for these tasks is wide open. That said, engineered design is predicated on the availability of fundamental data and theory. The instrument we have built is providing information vital to innovate and execute superior technologies that support diverse US Army missions. These studies (that, ultimately, promote device efficiency) are more critical than ever since the US armed forces must continually evolve to widen is overall missional scope while decreasing its resource and personnel footprint.

While ILs have tremendous potential to push technological boundaries, a great amount of additional characterization data is required to understand and then fine rune these materials for applications that often demand balancing competing variables/properties. For example, ILs utilized as electrolytes often exhibit low conductivity relative to aqueous electrolytes (chiefly due to the higher viscosity of ILs); however, substituting to weaker coordinating anion in attempt to increase conductivity may be detrimental to the solubility of the electrochemically active species of interest. While a great deal of progress has been made to identify classes/types of ILs that may be useful for a particular function, there remains much detail oriented work to characterize and engineer these systems for economically and technologically relevant purposes. Our research focus, interfacial characterizations of ILs at electrode surfaces, is a means to achieve important progress.

The recent advent (last 5 to 8 years) of commercially available tunable IR laser sources (e.g., QCL systems) is a means to push the temporal resolution of IR spectroscopy to new heights. In addition, great progress has been made in the commercial availability of focal plane array (FPA) IR cameras. In this report we detail the construction of a spectrometer system that will allow our group to (continue to) perform fundamental electrochemical characterizations of IL electrolytes at, for example, conductive carbon (i.e., graphene) surfaces in ways that document IL microstructure near the electrode surface. The new QCL system thus enhances and expands the scope of research that can be performed.

Summary of Results

Figure 1 shows an overview of the hyperspectral system that has been designed and built. In short, a Block Engineering QCL provides a bright beam of IR light that can be tuned across a wide range (5.4 – 12.8 µm). Reflective optical beam expanders (ROBE) expand and shape the IR beam. A Pike VeeMAX III optics system controllably directs IR light towards an attenuated total reflectance (ATR) crystal which serves as the 'window' into the electrochemical cell (ECC). Additional ROBEs bring IR light to the ICI 7320 IR FPA camera detector that is well matched (2.6 – 14 µm) for the output of the QCL. The setup is mounted on linear and rotating stages that enable a flexible setup for various experiments. Computer control syncs the QCL with the FPA detector while recording, sorting, and visualizing the data.

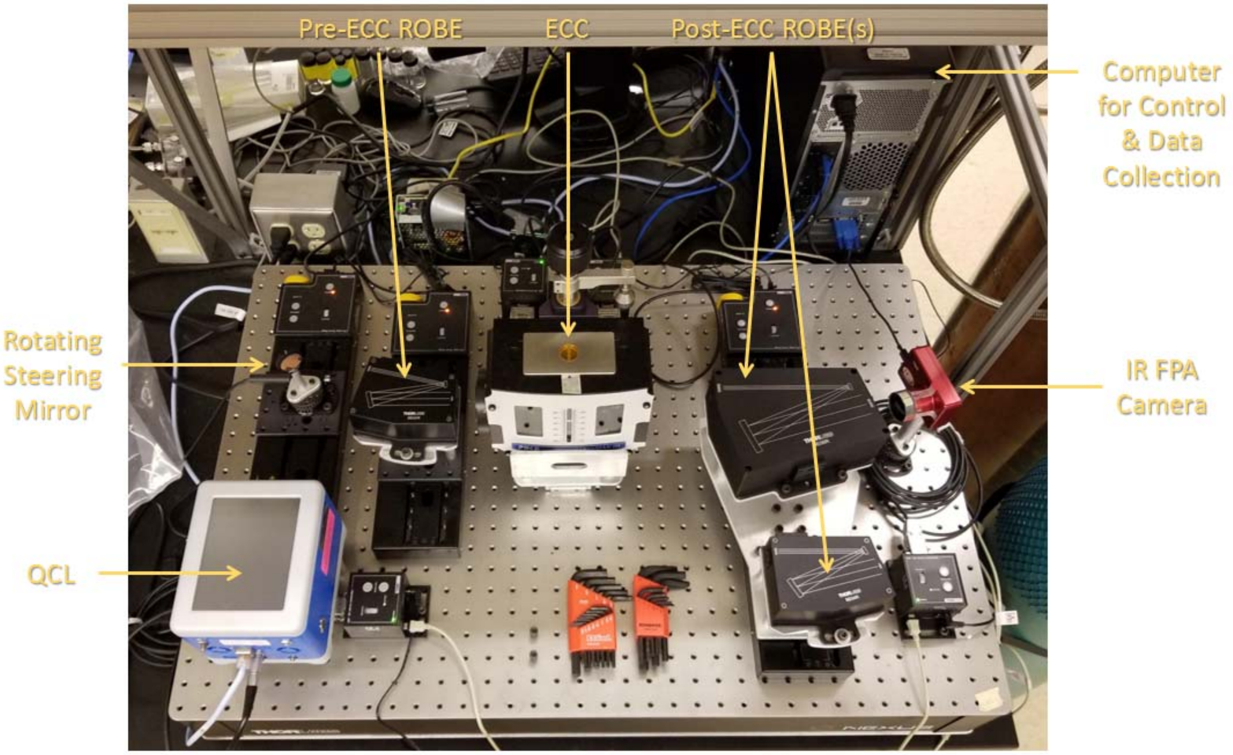

Figure 1: Image of the hyperspectral system. Infrared light is generated by the tunable quantum cascade laser (QCL) system. The beam is steered by a rotating mirror towards a reflective optical beam expander (Pre-ECC ROBE). The Pre-ECC ROBE is mounted on a sliding table for (optional) beam expansion prior to the electrochemical cell (ECC). Light is brought into the ECC by an adjustable reflective optics system (Pike VeeMAXIII) which includes the attenuated total reflectance (ATR) crystal. (Teflon ECC cap removed so that the ATR crystal is visible.) From there the IR laser beam can be expanded (optional) by additional ROBEs also mounted on a sliding table (Post-ECC ROBEs). An IR sensitive focal plane array (FPA) camera (detector) collects and records light from the ATR crystal. Hardware is linked by a computer control system that also collects data from the FPA camera. (Not shown is a cover which can mount to the optics bench and be purged with nitrogen to limit IR absorption from carbon dioxide and water in the atmosphere.

Figures 2 and **3** show several of the different configurations that are possible. All system components are mounted on an optical bench with precision linear and rotating stages that enable fine-tuned alignment.

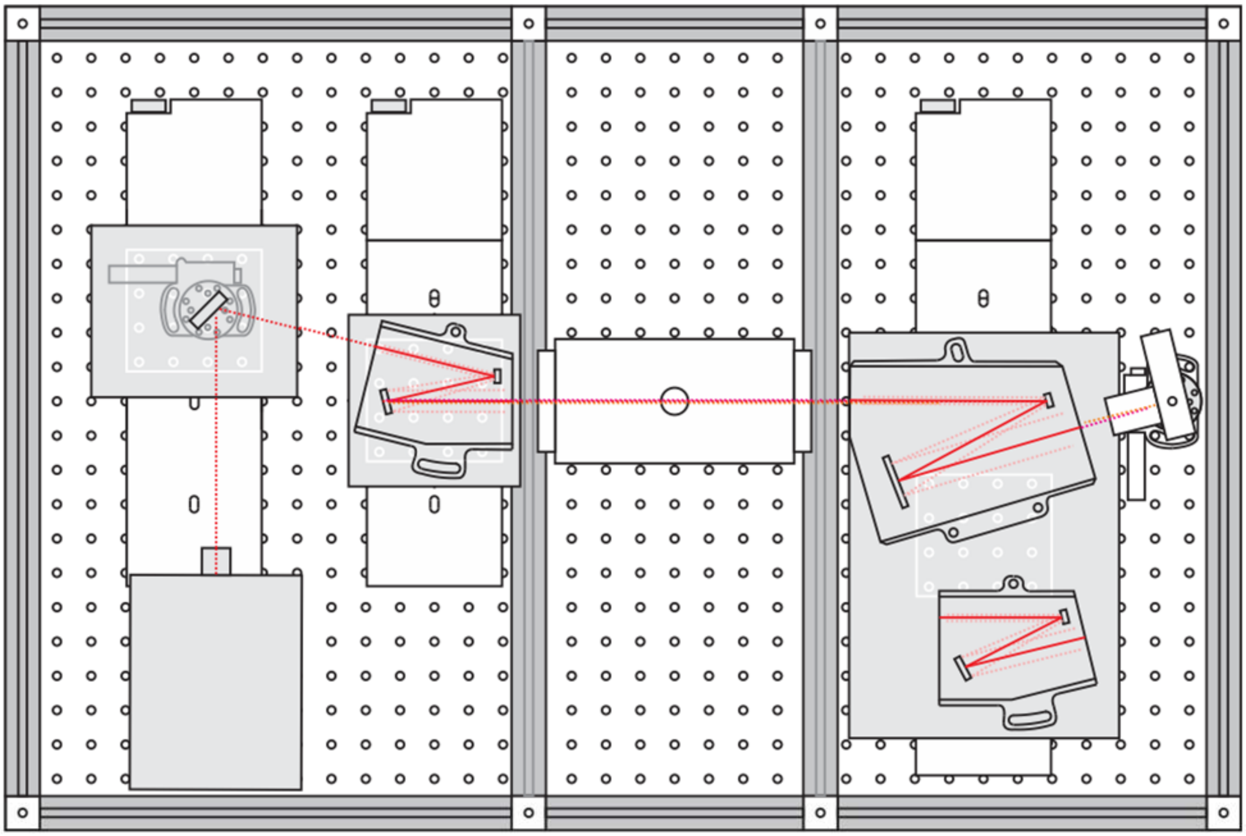

Figure 2: Above is a simplified illustration of the hyperspectral system (light path left to right) in its 'normal' configuration. (Similar to what is shown in **Figure 1**.) The beam path through various optical components is highlighted in red.

Figure 4 details the operating principals for SEIRA spectroscopy. IR light is directed through an attenuated total reflectance (ATR) crystal on to which a thin 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 SEIRA spectroscopy, thin 'island-like' films (but touching so as to be conductive) promote surface plasmon resonance that amplifies the absorbance of adsorbed species in addition to providing a larger interfacial surface area. If adsorbed species are present, IR modes perpendicular to the surface have enhanced IR absorptions (than for similar modes in the bulk solution). Thus individual species can be observed at or very near the surface and orientation data can be deduced.

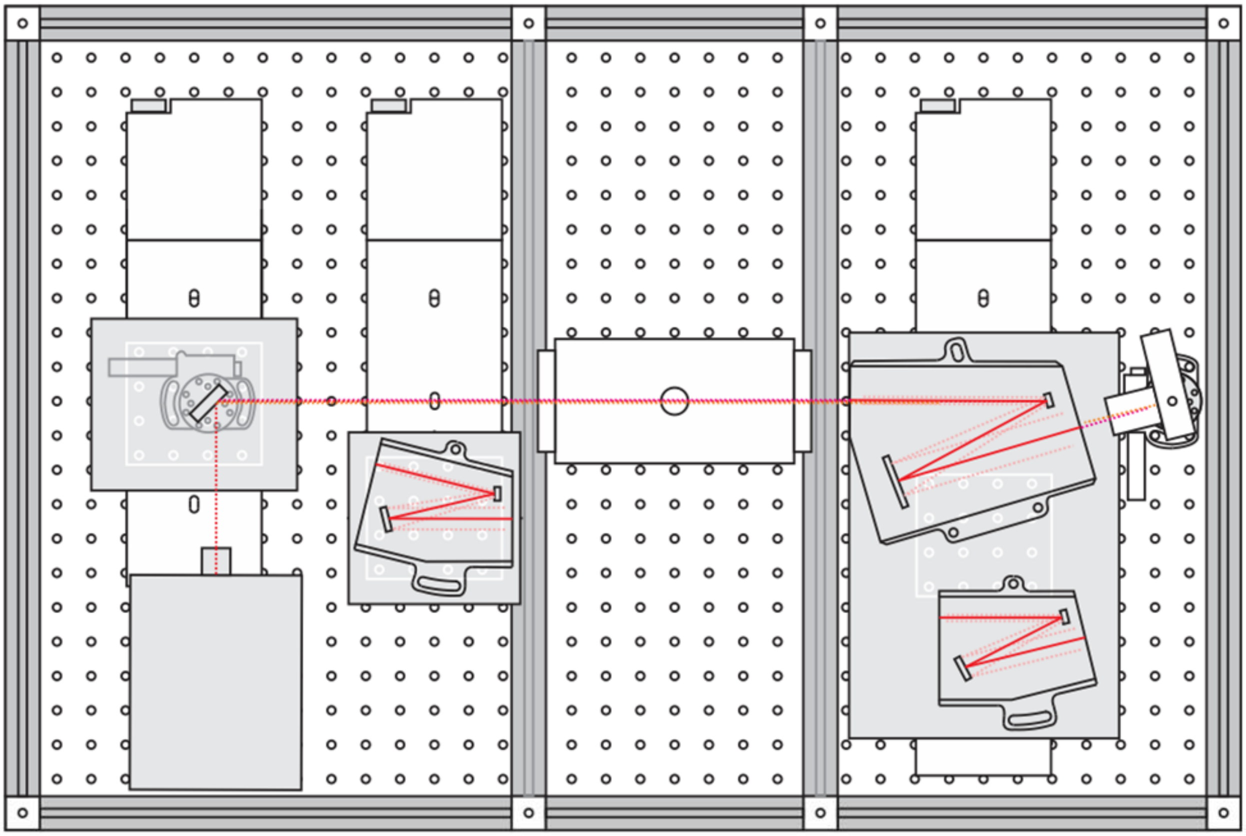

Figure 3: Above is a simplified illustration of the hyperspectral system (light path left to right). Pre-ECC ROBE removed from beam path to keep the laser spot size smaller and enable point detection sampling.

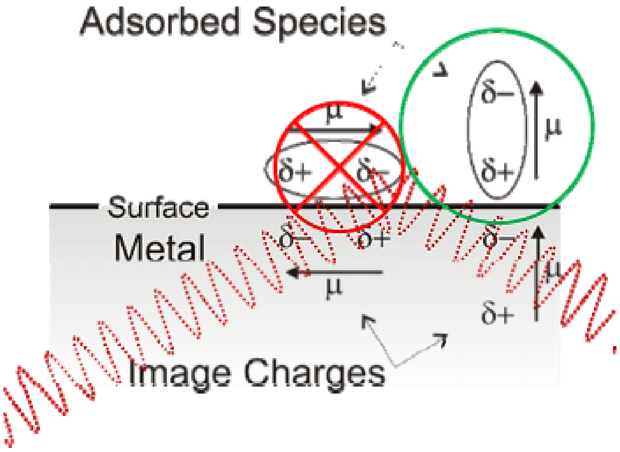

Figure 4: An illustration of the working principal of SEIRA spectroscopy. A thin conductive material is deposited on the ATR crystal and becomes an electrode of the ECC. The metal film is thin enough to transmit IR light from the QCL. IR active modes of molecules and ions near the conductive film either absorb or do not absorb light depending on their orientation and interaction with surface plasmon image charges (that arise from the motions of electrons within the conductive surface).

Figure 5 details how a Teflon top piece can be clamped on top of the ATR crystal (with thin film metal electrodes deposited by sputtering) forms the ECC. The top pieces can be custom fabricated to perform a number of types of experiments. The images in **Figure 5** show an arrangement for which seven different electrodes can be interrogated. (The seven individual holes isolate each electrode.) In this way individual electrodes are spectroscopically analyzed and effects due to hysteresis can be deduced since electrodes can be individually addressed and controlled by a multichannel potentiostat.

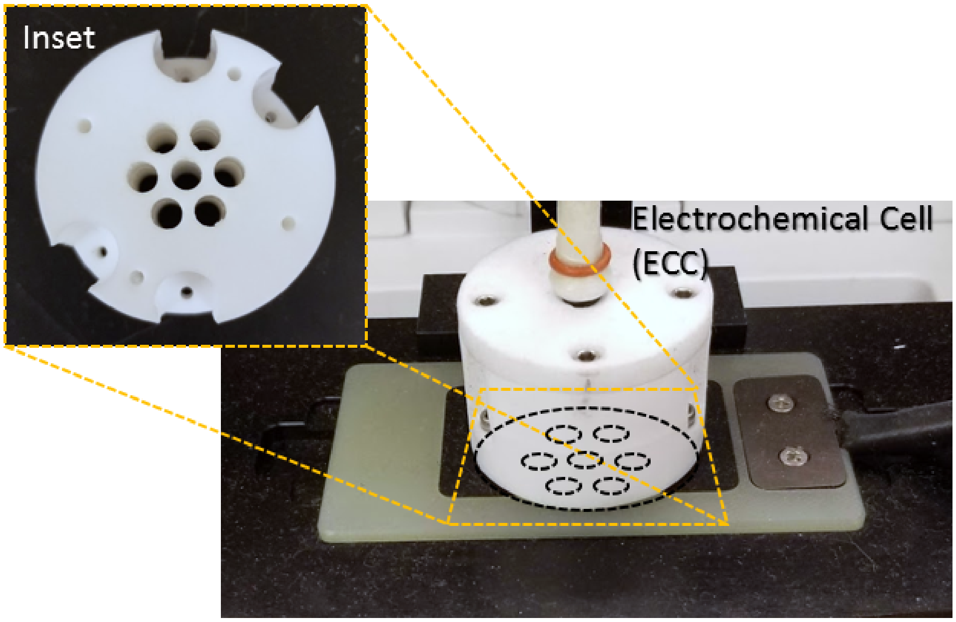

Figure 5: Picture of (one version of) the Teflon electrochemical cell along with a close up image (Inset) of the bottom of one version of the cell. The bottom of the particular ECC has 7 holes/chambers connected by channels that enable multiple experiments to be set up and interrogated.

Figure 6 is a conceptual illustration of a simplified experiment. Two different electrodes are illustrated being interrogated simultaneously by QCL illumination (λ_1) while the FPA detector collects data. Spectroscopic data from individual pixels of the FPA can be binned and two spectra independently generated. (The tunable QCL can be swept through different wavelengths of light while the camera records images for each wavelength to create a full spectrum analysis) **Figure 7** details that as signals are recorded and binned in time (t_1, t_2, …t_n), the time resolved spectrum is resolved.

The instrument described in this report is now being utilized to perform experiments analogous to that represented in **Figure 8**. Data in **Figure 8** are collected with a conventional spectrometer and are shown as a stack plot of SEIRA spectra for [EMIM][TFSI] at a sputtered gold electrode. Our group has observed qualitatively reproducible data with conventional spectrometer systems, but we have struggled to reproduce quantifiable data sets (e.g., the repeatable time constant for potential step experiments). With the ability to interrogate multiple systems simultaneously, multiplexed hyperspectral data may help to resolve complex hysteresis that may be in play for this system (and other similar systems).

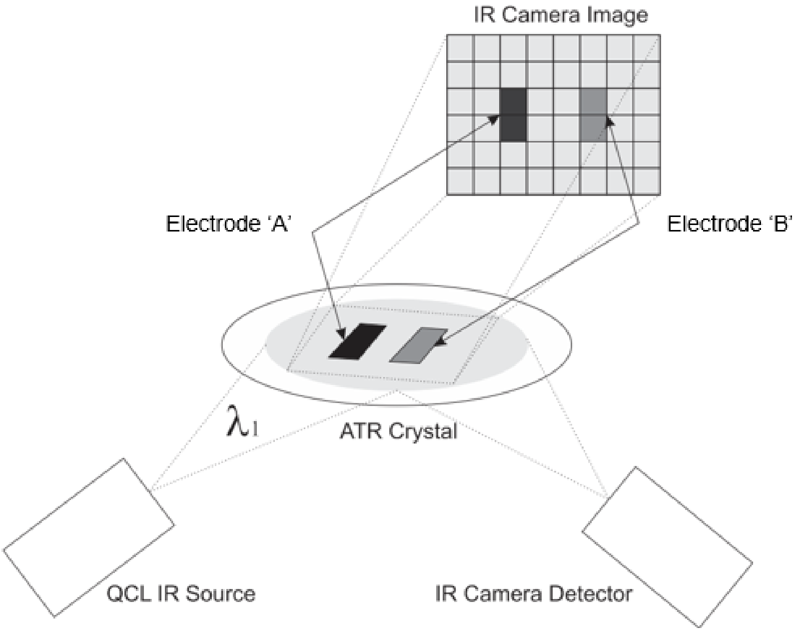

Figure 6: Simplified illustration of the basic operating principal of the hyperspectral system. Monochromatic IR laser light (λ_1) from the QCL is directed to the ATR crystal and the evanescent wave at the crystal surface interacts with species at or near the surface. The coherent light beam continues on to the IR FPA camera where the image is registered.

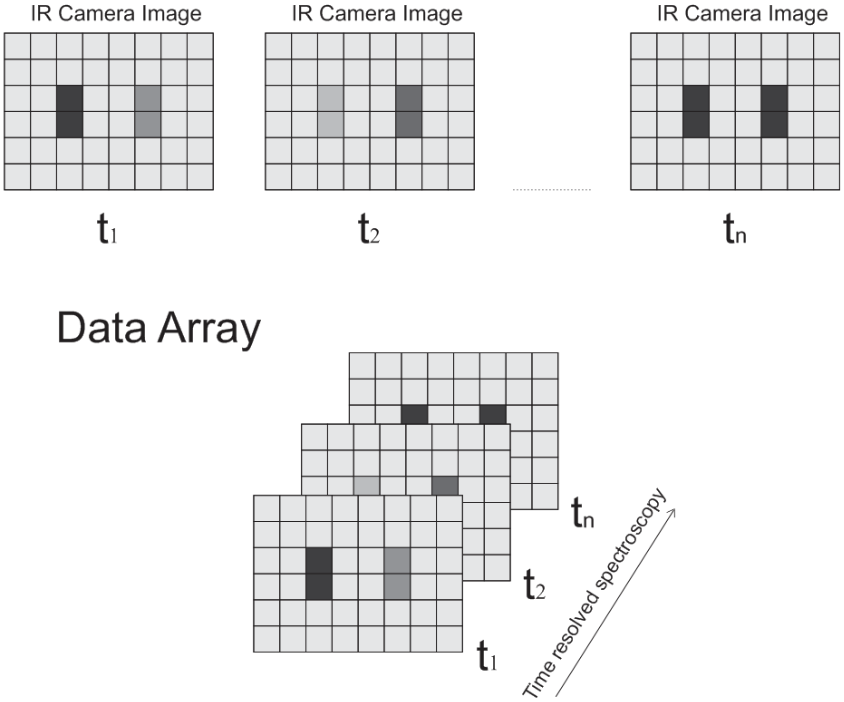

Figure 7: By repeating the basic operating principal illustrated in **Figure 6**, time resolved spectroscopy is stored and analyzed as multidimensional data arrays.

Figure 8 shows difference spectra collected after the first potential step (from -1.5 V to +0.8 V). Data are the difference spectra obtained by subtracting individual absorbance spectra collected at different times from a single background (subtractive) spectrum. As shown by the inset (upper left of **Figure 8**), the electrochemical cell was held at -1.5 V for ten minutes, then stepped to +0.8 V for ten minutes, then stepped back to -1.5 V for ten more minutes. The shaded regions denote the general 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$_2$) (8). Data show absorption peaks that correspond with the anion become more pronounced with time. These results are consistent with the idea that anion density should increase near the electrode as the potential is switched from negative to positive potential.

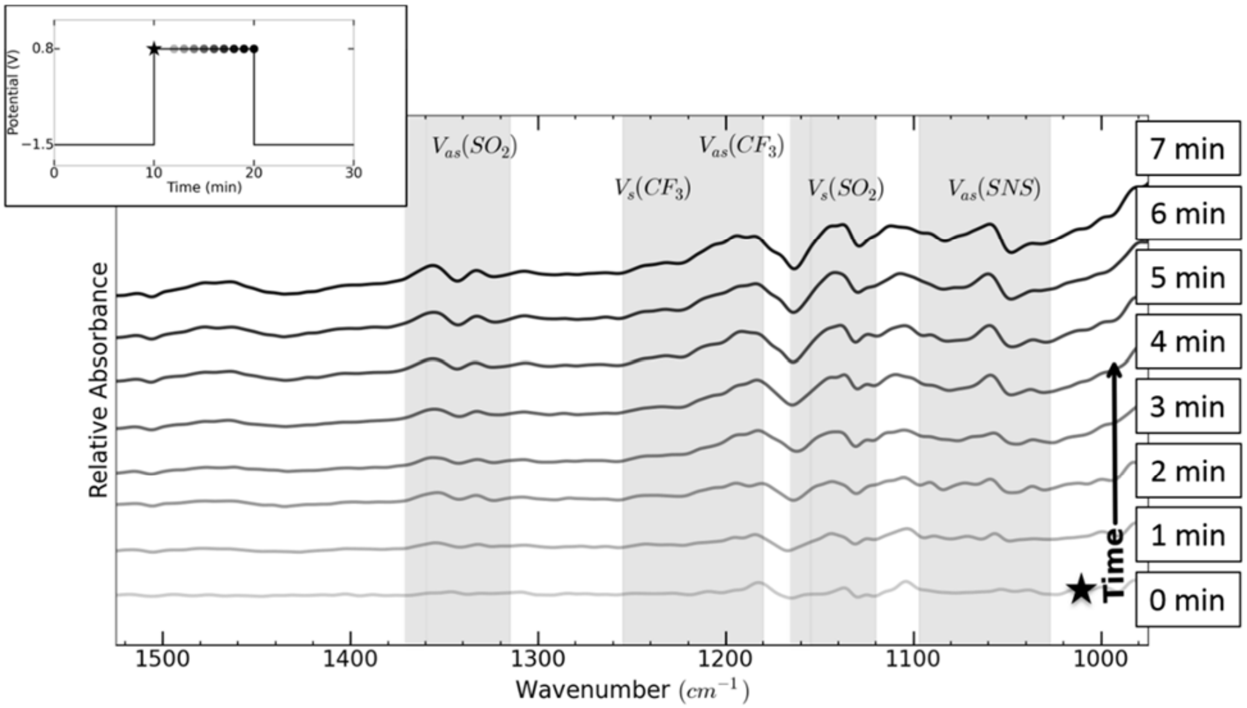

Figure 8: A stack plot of SEIRA difference spectra for [EMIM][TFSI] at a sputtered gold electrode.

In future work, our group will utilize the QCL-based system to gain a deeper insight into the behavior of IL electrolyte solutions as a function of electrochemical perturbation. In particular, we will continue to explore the time frames and mechanisms for hysteresis in IL systems.

Acknowledgments

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