SPECTROSCOPIC AND OPTICAL DIAGNOSTICS
FOR INVESTIGATIONS OF LIQUID ELECTROLYTES

by

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ABSTRACT

In this work, optical diagnostics are developed to investigate the electrochemical reactions and materials limitations of new battery technologies through in-situ and in-operando identification of species and measurements of species concentrations in liquid electrolytes.

Room Temperature Ionic Liquids (RTILs) are a promising type of new electrolyte material. RTILs have large electrochemical windows, low vapor pressures, and higher thermal stabilities than many organic electrolytes. The physical and electrochemical properties of RTILs are highly dependent on purity of the RTIL, and as a result considerable expense is added to the synthesis process by purification steps.

Here, the first quantitative optical diagnostics are presented for heated RTILs. These quantitative spectra are used to make in-situ spectroscopic measurements of the rate of decomposition of heated [EMIM][EtSO₄]. This study is the first in-situ optical investigation of the thermal breakdown of RTILs.

Quantitative UV-vis spectral data of [EMIM][TFSI] and a common impurity, MIM, were applied to develop an low-cost optical sensor to provide process control for the industrial production of [EMIM][TFSI]. Custom hardware was constructed and tested in order to establish a calibration curve and limit of detection for the sensor.

Quantitative spectroscopic techniques were also applied to measurements in a Na-Cu-I⁻ battery. Quantum chemical calculations were performed to estimate the UV-vis absorption spectrum of the CuI₂⁻ ion. A custom optically accessible transmission cell has been designed and tested using both electrochemical methods and UV-vis spectroscopy. The quantitative spectral data are used to develop optical diagnostics for in-operando quantitative measurements of species concentrations in the cell. Comparison of the optical concentration measurements and the cell current reveals the formation of CuI₂⁻ is slow compared to the formation of CuI.
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Research is creating new knowledge — Neil Armstrong
CHAPTER 1
INTRODUCTION: OPTICAL SYSTEMS AND SPECTROSCOPY

Electrical energy plays an increasingly large role in the modern world. As more countries industrialize and new technologies emerge, world demand for electrical energy continues to increase. As developing countries build electrical infrastructure and increase in wealth, many of their citizens have access to electrical appliances for the first time. Industrialization can therefore lead to explosive growth in demand for electrical energy. In rapidly industrializing China, the number of air conditioner units rose from 8 units per 100 households in 1995 to 106 units per 100 households in 2009 [1]. Overall, total worldwide demand for electrical energy is expected to double by the year 2050 [2].

In order to meet this demand, new energy sources are required. Renewable energy sources such as wind and solar energy have been promoted as solutions to the growing need for electricity [3, 4]. However, many renewable energy sources offer intermittent generation where capacity rises and falls with the availability of the energy source. In order to provide reliable power to customers, a load-leveling solution is needed. Load-leveling allows excess capacity during times of high energy availability or low demand to be used to generate electricity that is stored for later use through the means of an energy storage system [2, 5, 6].

Portable storage of electricity has also become increasingly important in the modern world. As more portable electronic devices enter the market, demand for safe, reliable, and compact energy storage is increasing [7]. At the same time, rising fuel costs and environmental concerns have given rise to a quickly growing market for electric vehicles that is driving demand for portable energy storage as well [8, 9].

Electrochemical storage methods such as rechargeable or secondary batteries are a widely used method of storing electrical energy. New electrolyte materials and battery chemistries for improved energy storage applications are an area of active research [10–12]. In order to
incorporate these new materials and chemistries into future electrochemical devices, they must be characterized. For example, when a new electrolyte material is developed, the properties such as the thermal stability and decomposition products must be known to ensure device safety and minimize the environmental impact of the device. For new battery chemistries, experimental measurements of reaction mechanisms, diffusion coefficients, and reaction kinetics allow computational models to optimize the design of potential devices.

In order to obtain the experimental data, diagnostic techniques which can measure variables such as species concentration, temperature, and other properties are needed. Optical diagnostic techniques offer several advantages for making measurements in electrochemical materials and systems. First, optical techniques are non-invasive. Optical methods interrogate a sample with a beam of light and do not rely on the use of a probe or sampling mechanism to collect data. The non-invasive nature of optical measurements allows optical methods to be used in-situ or in-operando to observe the behavior of materials and devices. Optical methods also provide complementary information to other measurement techniques such as electrochemical measurements.

1.1 Applications of spectroscopy to electrolytes

Optical spectroscopic methods have characteristics that are useful for studying energy systems. First, optical spectroscopy encompasses a wide range of techniques that may be tailored to interrogate different physical properties of the sample, such as species concentrations, temperature, or the bond structure of molecules in the sample [13]. In electrochemical systems, spectroscopy is often used to measure the concentrations of relevant electrochemical species [14]. Species concentrations are of interest in electrochemical systems because the concentration of electrochemical reactants or products determine parameters such as the cell voltage and maximum current density. The relationship between species concentrations and cell parameters will be discussed in Chapter 4. Optical spectroscopic techniques are also commonly used to characterize electrolyte materials, in order to gain insight into the properties of the electrolyte and how it will behave in an electrochemical device [15].
Optical spectroscopic techniques are used to address different measurement and sensing requirements. As we will discuss, optical spectroscopy may be used to identify and quantify species present in a sample. Spectroscopic techniques capable of measuring temperature, pressure, or other variables also exist [13, 16–18]. Here, optical absorption spectroscopy in the ultraviolet-visible (UV-vis) and infrared (IR) regions of the spectrum is applied to three applications in the field of electrochemical devices and materials. These applications are:

1. **Fundamental characterization of ionic liquid electrolytes.** As a promising new class of electrolytes and solvents for electrochemical devices and other applications, there is a demand for information on the thermal properties of ionic liquids. In particular, this work will examine the spectral properties of ionic liquids at elevated temperatures.

2. **Detection of impurities in ionic liquids.** Impurities have been shown to negatively impact the performance of ionic liquids for electrochemical applications. Quantitative spectral data may be used to measure the concentration of impurities in a sample using optical methods. This work will apply data collected using the spectral techniques in Chapter 2 to the development of a sensor to detect the presence of impurities in ionic liquids for industrial process control.

3. **In-operando quantitative optical measurements of species concentration in an optical battery.** Spectral measurements can be applied to full electrochemical devices, allowing for measurements to be taken during device operation, or in-operando. This work will conclude with measurements of species concentration in a sodium-copper-iodide cell with optical access.

In each of the above experiments, absorption spectroscopy is used to quantitatively measure concentrations of chemical species in liquid electrolytes. In order to understand the experimental methods used to make these measurements, it is necessary to develop the theory of how light interacts with a medium. The physical principles governing how light is
attenuated or augmented as it passes through a medium may be exploited to allow measurements of relevant physical properties of the electrolyte.

1.2 Light in an absorbing medium: The radiative transfer equation

Absorption spectroscopy relies on the physical phenomenon of optical absorption. As light travels through an absorbing medium, such as a liquid sample, the intensity of the light is attenuated by absorption and scattering. The intensity of the light may also be increased through the emission of backbody radiation, fluorescence, or stimulated emission. The intensity of light as it passes through the medium is described by the radiative transfer equation (Equation 1.1).

\[
\frac{dI_\lambda}{ds} = j_\lambda - \kappa_\lambda I_\lambda - \sigma_{s\lambda}I_\lambda + \frac{\sigma_{s\lambda}}{4\pi} \int_{4\pi} I_\lambda(\hat{s}_i)\Phi_\lambda(\hat{s}_i, \hat{s})d\Omega_i
\]  

(1.1)

In the above equation, \( I_\lambda \) is the intensity of the radiation along the path of integration \( s \). The subscript \( \lambda \) denotes that the value of \( I \) is a function of the wavelength of the radiation. \( j_\lambda \) represents radiation emitted along \( s \). \( \kappa_\lambda I_\lambda \) models the radiation absorbed by the medium. \( \sigma_{s\lambda}I_\lambda \) accounts for radiation lost to scattering, and \( \frac{\sigma_{s\lambda}}{4\pi} \int_{4\pi} I_\lambda(\hat{s}_i)\Phi_\lambda(\hat{s}_i, \hat{s})d\Omega_i \) describes the radiation contributed by multiple scattering events to the intensity at a point along \( s \). The radiative transfer equation allows the intensity to be calculated at any point along the path of integration. The different terms of the radiative transport equation represent various sources and sinks of radiation along the path \( s \) through a participating medium. The radiative transfer equation describes the intensity of radiation in most systems. For some systems, some of the source and sink terms in the radiative transfer equation are not significant. The following discussion of the terms of the radiative transfer equation and its component terms is summarized from *Radiative Heat Transfer* [19].

1.2.1 Emission

The term \( j_\lambda \) accounts for any increases in intensity due to the emission of radiation by the medium. \( j_\lambda \) is the emission coefficient for the participating medium. Particles in the medium
May emit radiation either as blackbody radiation or as spectral lines by transitioning from higher to lower quantized energy levels.

Emission from the medium is small and may be considered negligible under certain circumstances. For instance, when the medium is cold blackbody radiation is small. Depending on the wavelength range of interest and the desired level of accuracy in measurements or calculations, radiation intensity due to emission may be insignificant.

The intensity of blackbody radiation from a surface may be calculated from the Stefan-Boltzmann Law

\[ I_b = \frac{1}{\pi} \sigma T^4 \]  \hspace{1cm} (1.2)

where \( I_b \) is the intensity of blackbody radiation emitted from the surface, \( \sigma \) is the Stefan-Boltzmann constant \( (\sigma = 5.670 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}) \), and \( T \) is the absolute temperature of the surface in Kelvin. Equation 1.2 assumes that the surface is a perfect blackbody. For a sample at the maximum temperature in this study (200 °C), the intensity of the blackbody radiation \( I_b = 904 \text{ W} \cdot \text{m}^{-2} \) [20].

In order for the blackbody radiation from the sample to interfere with the operation of the FTIR spectrometer, the blackbody radiation must be collected by the spectrometer optics and focused onto the detector. Blackbody radiation is diffuse and radiates in all directions equally. The FTIR spectrometer is designed such that the beam from the light source is collimated in the sample compartment. Any blackbody radiation not traveling in the path of the collimated beam will be rejected by the spectrometer. Figure 1.1 shows a diagram of the sample compartment.

In order for a photon emitted by blackbody radiation to reach the spectrometer detector, the photon must be emitted within the beam cross section and travel in the same direction of the beam to the collection optic. The radiation exchange between the cross section of the beam at the cell window and the collection optic is given by

\[ q_{1-2} = I_b A_1 \cos(\theta_1) \omega_{2-1} \]  \hspace{1cm} (1.3)
where $q_{1-2}$ is the intensity of the radiation transferred from the cross section of the spectrometer beam on the cell (area 1) to the cross section of the spectrometer beam on the collection optic (area 2), $A_1$ is area 1, $\theta_1$ is the angle between the normal of area 1 and the optical axis between area 1 and area 2 ($\theta = 0^\circ$ in this case), and $\omega_{2-1}$ is the solid angle of area 2 as seen from area 1. $\omega$ is calculated as

$$\omega = \frac{A_2}{r^2}$$  \hspace{1cm} (1.4)

where $r$ is the distance between area 1 and area 2 for cases where $A_2/r^2$ is much less than 1 [20]. By combining Equations 1.3 and 1.4 and picking reasonable values of $A_1$, $A_2$, and $r$, we may estimate the amount of blackbody radiation that reaches the spectrometer detector. If the beam diameter $d$ is 5 mm, and the distance between the cell and the collection optic $r$ is 20 cm, then the optical power of the blackbody radiation reaching the detector is

$$q_{1-2} = 904 \times \pi (2.5 \times 10^{-3})^2 \times \cos (0) \times \frac{\pi (2.5 \times 10^{-3})^2}{2^2} = 8.6 \ \mu W$$  \hspace{1cm} (1.5)

This amount of blackbody radiation is small compared to the typical source optical power of $\sim 100$ mW of an FTIR spectrometer. Furthermore, the source in a FTIR spectrometer is modulated in time by the instrument’s interferometer, and filtering is used to remove any noise which does not arrive on the signal’s carrier frequency. This filtering scheme enhances the signal to noise ratio of the spectrometer and rejects the blackbody radiation. Therefore,
the emission of blackbody radiation for samples in this study may be neglected for spectra taken with the FTIR spectrometer.

In order to determine the significance of blackbody radiation for the UV-vis, we can examine the wavelength of the blackbody radiation emitted by the sample. As the temperature of the sample increases, the wavelength of peak blackbody emission decreases according to Wien’s Displacement law.

\[ \lambda_{\text{max}} \cdot T = 2898 \mu \text{m} \cdot \text{K} \]  

For a sample at 200 °C, peak blackbody emission occurs at \( \sim 6.1 \mu \text{m} \). The range of the Maya 2000+ Pro UV-vis spectrometer is 165-615 nm, so blackbody radiation in the UV-vis may be neglected.

Emission may also occur when molecules in a sample transition from an excited state to a lower energy level. Molecules are excited from the ground state by absorption of photons from the spectrometer light source in spectroscopy. The energy absorbed by the molecules must be transferred elsewhere for the molecule to return to the ground state. The molecule may release this energy through several different mechanisms. Emission of a photons through processes such as florescence, spontaneous emission, and stimulated emission increases the intensity of radiation along the path \( s \). However, excited molecules may release energy through other processes not involving the emission of a photon. These processes are collectively known as quenching. In samples with a high density, such as liquids, collisional quenching greatly reduces the intensity of emission. Collisional quenching occurs when an excited molecule transfers energy to a nearby particle through a physical collision, dissipating the energy as heat [21].

In the samples studied in this work, quenching dominates any emission due to the low intensity light sources used to illuminate the sample. As the population of excited molecules in the sample is small compared to ground state molecules, the excited molecules collide with ground state molecules before emitting a significant amount of radiation.
1.2.2 Scattering

In a participating medium, radiation may be scattered by interactions between the radiation and the particles of the medium. Three primary physical processes take place when radiation interacts with particles. First, the path of the radiative photon may be changed by reflection of the photon on the particle surface. Second, the photon may penetrate into the particle and be refracted. Finally, the photon may not directly contact the particle but still alter its path due to diffraction. Collectively, these processes are known as scattering, because they all involve a photon changing direction due to interactions with the medium. The oscillating electric field of incident light induces oscillating dipole moments on the surface of the particle. These dipoles in turn re-emit electromagnetic waves, leading to reflections and diffraction [22, 23]. Figure 1.2 shows the particle-radiation interactions that are known as scattering.

Figure 1.2: Possible interactions between a particle of radius $a$ and incident radiation, $I_\eta$. Radiation may be reflected, refracted or diffracted by the particle. Radiation may also be absorbed by the particle, which will be discussed in a later section.

Scattering behavior is dependent on the wavelength of the incident radiation and the size of the scattering particles. The relative size of the particle to the wavelength of the incident radiation may be described by a size factor:
Depending on the size factor, scattering may follow one of three regimes:

- When $x \ll 1$, Rayleigh scattering is the dominant scattering mode. Rayleigh scattering is a common occurrence in the atmosphere, where the small gas particles scatter light from the sun. The intensity of Rayleigh scattering is proportional to $\lambda^{-4}$, so shorter wavelengths are scattered more than longer wavelengths. As blue light has the shortest wavelength of the visible spectrum, the sky appears blue due to the effects of Rayleigh scattering.

- When $x \approx 1$, the scattering regime is known as Mie scattering.

- When $x \gg 1$, the particle may be treated as an ordinary surface such as a blackbody or gray surface. Geometric optics may be used to describe these interactions.

Scattering may attenuate or increase the intensity of radiation passing through the medium. Scattering may direct a photon out of the path $\hat{s}$, as shown in Figure 1.3. In the radiative transfer equation (Equation 1.1), scattering is accounted for by two terms. The first represents the attenuation of radiation by scattering. This attenuation is represented by a scattering cross-section, $\sigma_{s\lambda}$, which represents the probability that an incident photon will be scattered by a particle in the control volume out of the path $s$, resulting in attenuation. The second term accounts for in-scattering, that is scattered from other paths into the path $s$. These scattering interactions increase the intensity of radiation along $s$.

### 1.2.3 Absorption

Light traveling through a participating medium may be absorbed by the component molecules of the medium. Several different physical processes at the molecular level are capable of absorbing incident photons. In all cases, photon absorption is due to quantized energy level transitions present in the molecule. The following discussion on energy transitions
Scattering may divert photons from the path \( s \) and reduce the intensity of radiation at a given point along \( s \). However, scattering may also direct radiation into the control volume at the given point and increase the intensity.

In molecules and absorption is summarized from *Fundamentals of Molecular Spectroscopy* [13]. A molecule with two energy levels, \( E_1 \) and \( E_2 \), has a possible transition of energy \( \Delta E = E_2 - E_1 \) (Figure 1.4).

From the energy of the transition, the frequency of a photon with the same energy may be calculated using the relationship developed by Max Planck:

\[
\Delta E = h \nu
\]

where \( h \) is Planck’s constant \( (h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}) \) and \( \nu \) is the frequency of the photon with energy \( \Delta E \). A molecule may absorb a photon of energy \( \Delta E \) to jump from energy level \( E_1 \) to \( E_2 \). The molecule may also emit an identical photon to jump from the higher energy level to the lower energy level. Different energy level transitions with different values of \( \Delta E \) are therefore associated with different characteristic wavelengths.
Figure 1.4: A molecule with a transition between two energy levels, $E_1$ and $E_2$, may absorb an incident photon of energy $\Delta E = E_2 - E_1$.

The electromagnetic spectrum includes a wide range of different transition mechanisms. Figure 1.5 shows the electromagnetic spectrum and the transition mechanisms found in each region of the spectrum. At the low energy end of the spectrum, long wavelength photons such as radio waves are found. These photons may be used to probe spin transitions through the techniques of nuclear magnetic resonance (NMR) spectroscopy and electron spin resonance (ESR) spectroscopy. NMR spectroscopy measures the energy of nuclear spin transitions, which is useful for determining the structure of molecules. Photons associated with nuclear
spin transitions may also be used for imaging, such as in medical magnetic resonance imaging (MRI) [24]. ESR spectroscopy probes spin transitions of electrons in a material. ESR spectra may be used to investigate crystal defects and materials with unpaired electrons [25].

In the microwave region of the spectrum, absorption is due to rotational transitions. Rotational spectroscopy is able to differentiate molecules with different moments of inertia, but not able to resolve the internal structure of the molecule since rotational transitions are energy transitions of the whole molecule. In the infrared region of the spectrum, the transitions probed are associated with the combined rotational and vibrational, or ro-vibrational, energy levels of molecular bonds [13].

1.2.4 Ro-vibrational transitions: Infrared absorption

Molecular bonds between atoms behave as anharmonic oscillators (Figure 1.6). The bond vibrates around an equilibrium internuclear distance $r_0$. As the separation between the two nuclei becomes large, the energy of the bond approaches the bond dissociation energy ($E_{\text{BDE}}$). Therefore if the bond absorbs enough energy, the nuclei will separate and the bond will break. Like all forms of molecular energy, the vibrational energy is quantized. These vibrational states are combined with rotational states. Each vibrational state has several vibrational states with slightly higher or lower energies. In spectroscopy, these rotational states may be seen as a collection of closely spaced peaks. Infrared photons may be absorbed or emitted in order for the bond to change energy levels between different ro-vibrational states.

Figure 1.6 shows some possible infrared absorption transitions. These transitions are characteristic of specific bonds, such as C–C, C–H, or C=H bonds. Because each type of bond has a group of characteristic transitions and photons, infrared spectroscopy is a powerful tool for identifying molecules. Different bonds may be quickly identified from an infrared absorbance spectrum, allowing researchers to identify molecules. Figure 1.7 shows some of the possible vibrational modes of water. Each vibrational mode has a different energy level. The transitions between these energy levels have different characteristic photons with energy corresponding to the difference in energy between energy levels.
1.2.5 Electronic transitions: UV-vis absorption

Ultraviolet and visible absorption lines are characteristic of electronic transitions in the absorbing molecule. In a molecule, individual atomic orbitals overlap to form molecular orbitals. The shape and energy of molecular orbitals is dependent on the molecular geometry and the type of atoms in the molecule. Since both the molecular geometry and types of atoms in the molecule determine the energy of the molecular orbitals, the wavelengths absorbed by electronic transitions are characteristic of specific types of molecules. UV-vis spectroscopy may therefore be used to identify and quantify species.

When a molecule is excited from the ground state, the electrons in the molecule transition from lower energy molecular orbitals to higher energy orbitals. Molecules may be excited by interactions with photons. Molecules may either absorb a photon to increase their energy level or emit a photon to return to a lower energy level. Figure 1.4 shows a schematic of the
process. The energy required to excite a molecule electronically, $\Delta E$, generally corresponds to photons in the UV-vis region of the spectrum.

1.3 Light in a purely absorbing medium: The Beer-Lambert Law

The intensity of light entering the sample, $I_0$, is related to the intensity of light exiting the sample, $I$, by the **Beer-Lambert Law** (Equation 1.22). In order to derive the Beer-Lambert Law, we will consider light propagating through a one dimensional absorbing medium (Figure 1.8).

In Figure 1.8, light propagates along the $z$ axis. The intensity of the light entering the sample at $z = 0$ is defined to be $I_0$. The intensity of light exiting the sample at $z = L$, where is $I$. $L$ is the distance the light travels through the sample, known as the **pathlength**.

In order to determine the relationship between $I$ and $I_0$, we will define a thin slab control volume of thickness $dz$ and an area $A$, which is normal to the $z$ axis. The amount of light that is absorbed in the control volume, $dI(z)$, can be expressed as a function of the amount of light entering the control volume and the probability that any given photon is absorbed in the control volume.
Figure 1.8: Light propagating through an absorbing medium is attenuated as molecules (red dots) absorb individual photons. The absorption cross-section associated with the absorbing molecule is given as $\sigma$, and the intensity of the light passing through the sample, $I$, is integrate over the pathlength of the sample to yield the Beer-Lambert Law.

$$I - I_0 = d(I(z)) = -P I(z) \quad (1.9)$$

In this equation $P$ represents the probability that a photon traveling through the control volume will be absorbed. The sign in Equation 1.9 is negative to indicate that light is lost in the control volume when it is absorbed by a molecule. To solve Equation 1.9 in terms of measurable quantities, we will now examine $P$, the probability of a photon being absorbed in the control volume.

A photon will be absorbed in the control volume if it strikes a molecule in the control volume rather than passing through a “clear opening”. The probability of the photon being absorbed is therefore the ratio of area of the control volume occupied by molecules to the total area of the control volume.

$$P = \frac{A_{\text{mol}}}{A_{\text{total}}} \quad (1.10)$$
The assumptions we have made to derive the Beer-Lambert Law are valid for many real substances and solutes. However, there are limitation to the assumptions made in the course of this derivation of the Beer-Lambert Law. Here, the probability will be visualized geometrically a ratio of two areas. In order to calculate this probability, we must know both areas in the ratio. We have already defined \( A_{\text{total}} \) as \( A \). To calculate \( A_{\text{mol}} \), we will define a new quantity, \( \sigma \), the \textbf{absorption cross-section}. The absorption cross-section is expressed as an area per molecule. It is important to understand that the absorption cross-section is not a physical cross-section, but an abstract representation of the probability that a molecule will absorb a photon. For example, the absorption cross-section for a molecule in the infrared region of the spectrum is dependent on the polarity of the molecular bonds in the molecule. However for the visible and ultraviolet regions of the spectrum, the absorption cross-section is dependent on the electronic structure of the molecule. The factors which determine this probability are complex, but ab-initio quantum calculations may be used to estimate the absorption spectrum of a molecule. An overview of these methods is presented in Chapter 4. When we apply to concept of the absorption cross-section, Equation 1.10 then becomes:

\[
P = \sigma \frac{N}{A}
\]  
(1.11)

where \( N \) is the number of molecules in the control volume. However, the quantity \( N/A \) is difficult to use in practical situations. \( A \) is arbitrarily defined and counting the number of molecules in a given area is difficult. We would prefer to work with the more familiar quantity concentration, which is the number of molecules per unit volume. We can express this volume in terms of the dimensions of our control volume.

\[
C = \frac{N}{V} = \frac{N}{A \, dz}
\]  
(1.12)

It is now possible to rearrange Equation 1.12 into a form which can be substituted into Equation 1.11.

\[
C \, dz = \frac{N}{A}
\]  
(1.13)
Substituting into Equation 1.11 yields:

\[ P = \sigma C \, dz \quad (1.14) \]

Now that we have established the probability that a photon will be absorbed in the control volume, we can substitute the expression for \( P \) (Equation 1.14) into Equation 1.9.

\[ d(I(z)) = -\sigma C \, I(z) \, dz \quad (1.15) \]

We are now presented with an ordinary differential equation with separable variables. We now separate the variables and integrate over the full pathlength of the sample.

\[ \frac{dI}{I(z)} = -\sigma C \, dz \quad (1.16) \]

\[ \int_{I(z)=I_0}^{I(z)=I} \frac{dI}{I(z)} = \int_{z=0}^{z=L} -\sigma C \, dz \quad (1.17) \]

Once the limits of integration are enforced, the expression is easily simplified and rearranged to yield the Beer-Lambert Law (Equation 1.22).

\[ \ln \left( \frac{I(z)}{I_0} \right) \bigg|_{z=L}^{z=0} = -\sigma C \, z \bigg|_{z=0}^{z=L} \quad (1.19) \]

\[ (\ln(I)) - (\ln(I_0)) = (-\sigma C \, L) - (-\sigma C \, 0) \]

\[ -\ln \left( \frac{I}{I_0} \right) = \sigma C \, L \quad (1.21) \]

In the above equation, the concentration, \( C \), is the number of molecules per unit volume. While this is a valid way of expressing the concentration, for most practical applications it is convenient to define concentration in units of moles per liter, which is known as the molar concentration or molarity, \( c \). To use the molar concentration in the Beer-Lambert law, we will replace the absorption cross section with the molar absorptivity coefficient, \( \epsilon \). The molar absorptivity coefficient is commonly expressed in units of \( \text{L-mol}^{-1} \cdot \text{cm}^{-1} \), which is dimensionally equivalent to the absorption cross section. Thus the Beer-Lambert law becomes
\[- \ln \left( \frac{I}{I_0} \right) = \epsilon(\lambda, T) c L \] (1.22)

Equation 1.22 allows quantitative measurements of species concentrations and temperature from transmission measurements. The light absorbed by a sample is directly related to the concentration of a molar species in that sample. The molar absorption coefficient is also a function of the temperature of a sample. If the temperature dependent molar absorption coefficient, \( \epsilon \), is known, measurements of the sample temperature may be made optically. Given the pathlength and molar absorption coefficient of the species, the concentration of the species in the sample can be measured optically. Furthermore, \( \epsilon \) is a function of wavelength and a material property that is unique to different species. 1.24 shows the absorption cross-sections of two species added together in a mixture. By reexamining the probability of a photon being absorbed in the control volume, we will show that absorption cross-sections of the species add linearly.

Figure 1.9: Absorption cross-sections sum in a linear fashion in a mixture. In a pure substance (a), the probability of a photon being absorbed is given by the ratio of area occupied by molecules to the total area of the control volume, \( P = \sigma C \, dz \). In a mixture (b), the area occupied by molecules is the sum of the area occupied by each of the molecular species, so the probability that a photon will be absorbed becomes \( P = \sum \sigma_i C_i \, dz \).

In a mixture, the probability that a photon will be absorbed in the control volume is still the ratio of area occupied by absorbing molecules to the total area of the control volume. However, now the area occupied by absorbing molecules is the sum of the areas occupied
by each individual species of \( n \) total species. Summing the areas to arrive at the total probability is valid so long as the absorption cross-section of a given molecule is independent of the other molecules. In our geometric analogy, independence means that the molecules cannot overlap. Thus the probability of a photon being absorbed in the control volume (Equation 1.14) becomes:

\[
P = \sum_{i=1}^{n} \epsilon_i c_i \, dz
\]  

(1.23)

After substituting the new probability into Equation 1.9 and solving, we arrive at the Beer-Lambert Law for mixtures.

\[
-\ln \left( \frac{I}{I_0} \right) = \sum_{i=1}^{n} \epsilon_i c_i L
\]  

(1.24)

Since the absorption cross-section of a species is dependent on the structure of the species in question, we must also examine the possibility that interactions between species in a mixture may affect the absorption cross-section of a species. In a liquid mixture interactions between solvents and solutes may form structures such as solvation shells and water clusters that may change the absorption spectrum of the species in question. One well-researched example of this phenomenon is the charge transfer to solvent spectrum. Charge transfer to solvent spectra arise in solutions of anions in polar solvents, such as water. Solvent molecules surround the anion, forming a solvation shell. The extra electron of the anion becomes delocalized and may travel through the solvation shell, leading to a new absorption spectrum in the ultraviolet and visible regions of the spectrum [26, 27]. Interactions between charged species in a liquid, such as the cations and anions of an ionic liquid, can also lead to complex interactions that change the absorption spectrum of the individual species [28]. As a result, spectral measurements of single components which are to be used in a measurement of a mixture containing that component should be checked to confirm that the absorption cross-section of the species in question adds in a linear fashion with the other components in the mixture.
Even with some limiting cases, the Beer-Lambert Law is a powerful tool for studying transparent samples. Once the absorption cross-section of a molecule is known, the concentration of that molecule in a sample may be determined from the measured absorbance of the sample. Furthermore, since the absorption cross-section is a function of wavelength and adds linearly for multiple components in many cases, multiple components can be measured simultaneously. Also, since the measurement relies on light transmitted through the sample, the sample may be investigated non-invasively and remotely. These characteristics of the measurement make optical absorbance an ideal method for in-situ and in-operando measurements.

Throughout the remaining chapters of this thesis, the application of the Beer-Lambert Law to sensing in electrochemical systems will be discussed. Through the use of the Beer-Lambert Law, it will be shown that quantitative measurements of electrochemical systems and materials is possible in a non-invasive way.
CHAPTER 2
QUANTITATIVE ABSORPTION SPECTRA OF HEATED
1-ETHYL-3-METHYLIMIDAZOLIUM ETHYLSULFATE AND IN-SITU OPTICAL
MEASUREMENTS OF THERMAL BREAKDOWN KINETICS

Room temperature ionic liquids (RTILs) have been the subject of extensive research in recent years. These salts that melt near room temperature display unique chemical and material properties and are applicable to a wide range of industrial applications. RTILs have been applied in electrochemistry due to their wide electrochemical windows and high ionic conductivity. RTILs also show promise as industrial lubricants [29, 30], and are also used as environmentally friendly solvents due to their low vapor pressure [31–33].

The high thermal stability and low vapor pressures of RTILs relative to other organic solvents has lead to interest in the use of RTILs in a variety of industrial and electrochemical applications. For example, biomass processing applications may use a heated RTIL to dissolve cellulose [34–36]. Electrochemical devices, where a RTIL may be used as an electrolyte, operate at elevated temperatures under heavy loads [37–39]. In battery applications, electrolytes that are stable at high temperature are required to prevent performance loss and to mitigate fire risks. RTILs have been investigated as alternative electrolytes which improve the safety of lithium ions batteries [40–42]. Some catalytic applications of RTILs take place at elevated temperatures [43–45]. Given the high cost of RTILs, industrial processes must efficiently recycle the RTILs in order to make the use of RTILs economical. Thermal degradation of the RTIL in an industrial process would have significant economic implications [46]. In order to incorporate ionic liquids into new designs, it is desirable to understand the thermal stability and physical properties of ionic liquids at elevated temperatures. Therefore, investigating the properties and stability of RTILs at temperatures up to \(\sim 100 \, ^\circ C\) is an area of active research [47–51].
Vibrational spectra from the infrared (IR) region of the spectrum have been used to investigate the structure and intermolecular interactions of RTIL molecules [52–55]. RTILs also display some absorption features in the ultraviolet and visible (UV-vis) regions of the spectrum. The UV-vis absorption spectrum of RTILs has been shown to be useful for detecting impurities in samples of RTILs [55, 56].

To date, most published RTIL optical absorption spectra have been qualitative in nature, and to the best of the authors’ knowledge no spectra are available for RTILs at elevated temperatures. It is the aim of this work to investigate the spectral properties of the RTIL 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][EtSO$_4$]) in the IR and UV-vis regions of the spectrum between 30 °C and 100 °C and to provide quantitative absorption data for this RTIL. These spectra may be used to develop in-situ and in-operando non-invasive diagnostics for systems based on [EMIM][EtSO$_4$]. These spectra may also be used to investigate the fundamental structure and properties as well as the kinetics of the thermal degradation of [EMIM][EtSO$_4$], as is demonstrated in this work.

2.1 Attenuation in optical cells

As discussed in Chapter 1, light traveling through a medium will be attenuated by absorption. By comparing a baseline spectrum with no absorption to the transmission spectrum ($I$) of the sample, we may use the Beer-Lambert law (Equation 1.22) to determine the molar absorptivity of the sample if the pathlength and concentration of the sample is known. In order to determine the molar absorptivity of a species, a representative baseline ($I_0$) is required. Reflection of incident light due to the sudden change in index of refraction at the window-air and window-liquid interface causes significant attenuation of the light passing through the cell. Attenuation due to reflection from the window surfaces must be identical in the blank and sample spectra to ensure that only attenuation due to absorption is captured in the absorption spectrum. If the optical losses resulting from these reflections are not taken into account, the attenuation will be attributed to absorption resulting in errors in the measurement of the molar absorption coefficient, $\epsilon$ [57].
For a sample contained in a transmission cell, we must also consider that reflections at the interfaces of the cell will attenuate the light beam of the spectrometer, as is shown in Figure 2.1. Liquid optical cells consist of two parallel windows which enclose a layer of the sample. In UV-vis measurements, the sample may be dissolved in a transparent solvent such as water or methanol and the pure solvent may be used as a baseline. In this case, the index of refraction of the pure solvent will closely match the index of refraction of a sample in dilute solution. The reflection losses will be similar in both the sample and the baseline, and when the Beer-Lambert law is applied to $I$ and $I_0$ the reflection losses will cancel.

![Figure 2.1: Light traveling through an optical cell is reflected at the air-window and window-liquid interfaces of the cell](image)

For IR measurements, solvents which are adequately transparent in the IR are not available; therefore spectra are collected of neat (pure) samples. This method presents an obstacle to obtaining a baseline spectrum since there is no pure solvent filled cell that can be used to correct for the reflective losses at the window interfaces. Using an empty cell would not provide a representative baseline due to the large difference in refractive index between most liquids and air. To successfully correct for reflection losses in the cell, a theoretical model of reflections in the cell may be used to model the interactions between the beam of the
spectrometer and the cell.

To model the reflection losses in the cell, the complex index of refraction is used to describe both refraction and absorption. The complex index of refraction is defined as

\[ \hat{n}(\nu) = n(\nu) + ik(\nu) \]  

(2.1)

where the real component, \( n(\nu) \), is the simple refractive index of the material and the imaginary component, \( k(\nu) \), describes the losses due to absorption in the sample. In quantitative spectroscopy, we are trying to measure \( k \) accurately because \( k \) is directly related to \( \epsilon \).

\[ \epsilon(\lambda) = \frac{4\pi k(\lambda)}{\lambda c} \]  

(2.2)

In the above equation, \( c \) is the molar concentration of the sample and \( \lambda \) is the wavelength of the light passing through the sample. Both \( \epsilon \) and \( k \) are functions of wavelength, so \( \epsilon \) is calculated point by point from \( k \). The complex index of refraction may be used to calculate the relationship between \( I \) and \( I_0 \) if both the real and imaginary components are known. Fresnel’s equations predict the behavior of a ray incident on an interface between two materials with different indices of refraction [57–59].

\[ r_s = \frac{\hat{n}_1 \cos \theta_I - \hat{n}_2 \cos \theta_T}{\hat{n}_1 \cos \theta_I + \hat{n}_2 \cos \theta_T} \]  

(2.3)

\[ t_s = \frac{2\hat{n}_1 \cos \theta_I}{\hat{n}_1 \cos \theta_I + \hat{n}_2 \cos \theta_T} \]  

(2.4)

\[ r_p = \frac{\hat{n}_2 \cos \theta_I - \hat{n}_1 \cos \theta_T}{\hat{n}_2 \cos \theta_I + \hat{n}_1 \cos \theta_T} \]  

(2.5)

\[ t_p = \frac{2\hat{n}_2 \cos \theta_I}{\hat{n}_1 \cos \theta_I + \hat{n}_1 \cos \theta_T} \]  

(2.6)

The geometry referenced by Fresnel’s equations is shown in Figure 2.2. The \( r \) and \( t \) terms are known as the amplitude coefficients and are for the reflected and transmitted light respectively. Each coefficient also has a subscript, either \( s \) or \( p \) which denotes the polarization of the light incident on the interface. \( s \) polarization is perpendicular to the page in Figure 2.2.
and $p$ is in the plane of the page. The intensity of the reflected and transmitted beams is given as

\begin{align}
R &= r^2 \\
T &= t^2 \left( \frac{n_2}{n_1} \right)
\end{align}

where $R$ and $T$ are the intensity of the reflected and transmitted beams respectively.

Figure 2.2: The interactions of a beam of light at an interface between two materials with differing indices of refraction. $I$ is the incident beam which strikes the interface at angle $\theta_I$. $R$ is the intensity of the reflected light and $T$ is the transmitted light. The angle at which the transmitted light exits the interface, $\theta_T$, may be calculated from Snell’s law.

If both the real and imaginary components of $\hat{n}(\nu)$ are known, $I_0$ may therefore be calculated using the Fresnel equations. In spectroscopy, we are presented with the inverse problem. $I$ and $I_0$ are measured experimentally, and the goal is to determine $k(\nu)$.

In order to determine $k(\nu)$ from experimental data, we will take advantage of another property of the complex index of refraction, causality. Kramers [60] and Kronig [61] determined that there is a causal relationship between the real and imaginary components of the complex index of refraction. This condition is sufficient to allow the use of the Hilbert
transform, a complex integral transform, to calculate the imaginary component from the real component. The inverse Hilbert transform may also be used to calculate the real component from the imaginary component. This application of the Hilbert transform gives rise to the Kramers-Kronig relations, which allow the calculation of a full complex function from either the real or imaginary component.

\[
\text{Im } \Omega(\omega) = \frac{1}{\pi} \text{p.v.} \int_{-\infty}^{\infty} \frac{\text{Re } \Omega(\omega)}{\eta - \omega} d\eta
\]

\[
\text{Re } \Omega(\omega) = -\frac{1}{\pi} \text{p.v.} \int_{-\infty}^{\infty} \frac{\text{Im } \Omega(\omega)}{\eta - \omega} d\eta
\]

(2.9)

(2.10)

In the above equations, \( \Omega \) is the complex function, \( \omega \) is the point at which the real or imaginary component of the function is being evaluated, and \( \text{p.v.} \) is an operator representing the Cauchy principle value of the integral [62].

The Kramers-Kronig relations may be applied to the problem of determining the \( k \) spectrum in spectroscopy. If we are able to determine the \( n \) spectrum, the \( k \) spectrum may also be determined. In an experimental absorbance measurement, attenuation due to \( n \) and \( k \) will be lumped together in the measurement of \( I \), so an iterative process is required to arrive at the final absorption spectrum, \( k(\nu) \).

To correct the dispersion errors in a measured spectrum the experimentally collected transmission spectrum, \( I \), and baseline spectrum, \( I_0 \), are used to calculated an apparent imaginary index of refraction, \( k_a \)

\[
k_a(\tilde{\nu}_0) = -\frac{\ln (I/I_0)}{4\pi \tilde{\nu}_0 L}
\]

(2.11)

where \( \tilde{\nu}_0 \) is the vacuum frequency in wavenumbers at which \( k_a \) is being evaluated and \( L \) is the pathlength of the sample.

A standard iterative process for correcting the reflection losses in an experimental spectrum has been established in the literature [57–59, 63–65]. At each iteration, an approximate \( k \) and \( n \) spectrum is refined until the spectrum converges. The iterative procedure followed
by the published software used for dispersion corrections in this work is given by

\[ k_i^{(j+1)} = k_i^{(j)} + (k_{a,i} - k_{aa,i}) \]  \hspace{1cm} (2.12)

where \( k_{aa,i} \) is the \( k \) spectrum calculated at iteration \( j \) from the \( n \) spectrum at iteration \( j \) with a Kramers-Kronig transformation. \( k_{a,i} \) is the experimentally measured absorption spectrum which does not change from iteration to iteration. The \( i \) subscript denotes the frequency data point at which the Kramers-Kronig transformation is being evaluated. \( k_i^{(j)} \) is the resulting \( k \) spectrum of the previous iteration. This iterative process runs until the \( k \) spectrum has converged. \( k(\nu) \) is tested for convergence by calculating a residual

\[ \delta = \sum_{i}^{m} \frac{|k_i - k_{aa,i}|}{m} \]  \hspace{1cm} (2.13)

where \( m \) is the number of data points, and \( i \) is the data point being evaluated. \( k_{a,i} \) and \( k_{aa,i} \) are as defined above. The \( k \) spectrum is said to be converged when \( \delta \) is smaller than a predetermined value.

To increase the speed of convergence and improve the accuracy of the correction, an implementation of a special form of the Kramers-Kronig transformation, the subtractive Kramers-Kronig transformation, is used. The subtractive Kramers-Kronig transformation relies on the real index of refraction being known accurately at fixed frequencies, which are known as anchor points [63]. The index of refraction at the anchor points is measured in cells with long pathlengths. The anchor points are selected at locations where absorption in the sample is small, so any attenuation in the light at that frequency is assumed to be due to reflections losses. The subtractive Kramers-Kronig transformation utilizing anchor points is given by

\[ n_i = n_r + \frac{2}{\pi} \left( \nu_i^2 - \nu_r^2 \right) \times \text{p.v.} \int_{-\infty}^{\infty} \frac{\nu k(\nu)}{(\nu^2 - \nu_i^2)(\nu^2 - \nu_r^2)} d\nu \]  \hspace{1cm} (2.14)

In the above equation, \( \nu_r \) is the anchor point location in wavenumbers. The subtractive Kramers-Kronig transform also has the advantage of higher accuracy for transforms performed on a finite interval by allowing a baseline correction to be applied to the spectrum.
Fresnel’s equations (Equations 2.4-2.6) may be used to calculate the shift in the spectrum baseline due reflections since the index of refraction is known at the anchor points. The baseline shift is interpolated between the anchor points and subtracted from the experimental absorbance spectrum.

The iterative process for performing dispersion corrections has been automated in computer programs, which are published and have been used to correct spectra for many studies of various samples [55, 65–68]. The established techniques and computer programs are applied here to measure the molar absorption coefficient, $\epsilon(\nu)$, of [EMIM][EtSO$_4$].

### 2.2 Experimental Methods

![Figure 2.3: The [EMIM][EtSO$_4$] ion pair in its lowest energy conformer. Adapted with permission from Dhumal et. al. [52]. Copyright 2011, American Chemical Society.](image)

[EMIM][EtSO$_4$] was obtained from Coorstek Fluorochemicals and used without further purification. All samples were stored and prepared in a dry nitrogen atmosphere. For IR measurements, spectra of neat [EMIM][EtSO$_4$] were collected by a Nicolet is50 FTIR with
0.5 cm\(^{-1}\) resolution and a spectral range from 450-7000 cm\(^{-1}\). The FTIR was purged with dry nitrogen to minimize the absorption from atmospheric H\(_2\)O and CO\(_2\). Three 32 scan averaged spectra were collected at each temperature and averaged together after correcting for reflection losses at the window-air and window-liquid interfaces with Keefe et. al.’s Kramers-Kronig programs [66]. The molar concentration of the neat [EMIM][EtSO\(_4\)] at temperature was calculated from density data measured by Fröba et. al. [69].

For measurement of UV-vis absorbance spectra, [EMIM][EtSO\(_4\)] was diluted in ACS spectrophotometric grade methanol (Sigma-Aldrich product number 154903). Samples were prepared and stored in a dry nitrogen environment. UV-vis spectra were collected with an Ocean Optics Maya 2000+ Pro spectrometer with a resolution of 0.25 nm and a spectral range from 165-615 nm. The light source used for the UV-vis measurements was a Ocean Optics DH-2000-DUV deuterium-halogen lamp. Extreme solarization resistant fiber optics were used to illuminate the sample and collect transmitted light. Due to attenuation by the fiber optics, UV-vis measurements were limited to wavelengths longer than 180 nm. Baseline spectra were collected at temperature using pure methanol. Due to the use of methanol as a solvent, temperatures were limited to below 60 °C to prevent boiling of the sample.

Sample temperatures were controlled with a Specac liquid transmission cell (Specac model number GS20501) paired with an electric heating jacket (Specac model number GS20730). The heating jacket controlled the sample temperature to ±1 °C. The cell was fitted with potassium bromide windows for IR measurements and Spectrosil B (UV silica) windows for UV-vis measurements. For pathlengths longer than 10 µm, a Teflon spacer was used to separate the windows. Cell pathlengths were measured from the interference fringes of the empty cells. For pathlengths shorter than 10 µm, a drop of [EMIM][EtSO\(_4\)] was placed between the windows and the pathlength was determined from a linear extrapolation of peak heights at 25 °C from samples with a known pathlength. In order to verify that the cell pathlength was constant with temperature, empty cells were heated and the pathlength was calculated from interference fringes. The cell pathlength was found to be constant over
the range of temperatures in this study. A list of cells used is shown in Table 2.1.

Table 2.1: IR cell pathlengths. All cells used KBr windows, and the sample in each cell was measured at 25, 50, 75, and 100 °C. For experiments where the ionic liquid was purposely degraded at high temperature, the 3400 cm⁻¹ anchorpoint was omitted due to the appearance of a peak at 3434 cm⁻¹ after significant degradation.

<table>
<thead>
<tr>
<th>Pathlength (µm)</th>
<th>Spectral Range (cm⁻¹)</th>
<th>Anchorpoints (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.5</td>
<td>1281-2641, 3400-7000</td>
<td>500, 2011, 2636, 3400, 3614, 5057, 6500</td>
</tr>
<tr>
<td>43.8</td>
<td>1281-2641, 3400-7000</td>
<td></td>
</tr>
<tr>
<td>36.5</td>
<td>1281-2641, 3400-7000</td>
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</tr>
<tr>
<td>3.8</td>
<td>500-1281, 2641-3400</td>
<td></td>
</tr>
<tr>
<td>6.6</td>
<td>500-1281, 2641-3400</td>
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</tr>
<tr>
<td>4.4</td>
<td>500-1281, 2641-3400</td>
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</tr>
<tr>
<td>5.8</td>
<td>500-1281, 2641-3400</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>500-1281, 2641-3400</td>
<td></td>
</tr>
</tbody>
</table>

2.3 UV-vis Spectra

UV-vis spectra were collected between 25 and 60 °C. No degradation of the ionic liquid is expected at these temperatures.

UV-vis spectra of [EMIM][EtSO₄] shows that the ionic liquid is mostly transparent with some slight broadband absorption in the visible wavelengths. This observation is consistent with reports of a slight yellow tint by researchers. This yellow tint is thought to be caused by trace amounts of heavier impurities present in RTILs at concentrations below the limit of detection of ion chromatography [70]. The largest absorption peak at 217 nm displays temperature dependence, decreasing with increasing temperature. There are also peaks at 193 nm and 233 nm. The UV-vis spectrum is shown in Figure 2.4.

Dhumal et. al. conducted time dependent density functional theory simulations which concluded that the peak near 217 nm is a result of the three lowest excited states of the lowest energy conformer of the ion pair. Dhumal et. al. also reported the peak location at around 226 nm [52]. However, the pathlength of the optical cell used by Dhumal et. al. was 1 cm with a neat sample. Early in this study, neat samples were determined to be opaque
below 225 nm even in cells with pathlengths less than 10 μm. The samples were therefore
diluted in methanol to allow measurements of absorbance at wavelengths below 225 nm. No
significant differences were observed between the neat and diluted samples.

![UV-VIS absorption spectrum of [EMIM][ETSO_4] (Figure 2.4)](image)

The UV-VIS absorption spectrum of [EMIM][ETSO_4]. The temperature range of the test
was limited due to the use of methanol as a solvent. Significant temperature dependence is
seen at the 217 nm peak.

### 2.4 IR Spectra

One of the key advantages of IR spectroscopy is the technique’s ability to probe the bond
structure of the sample molecule. Specific bond vibrations absorb characteristic frequencies
in the IR. Peak assignments for the [EMIM][EtSO_4] ion pair have previously been reported
[52, 54]. The ion pair is shown in Figure 2.3. The IR spectrum at 25, 50, 75, and 100 °C
is shown in Figure 2.5, with details in Figure 2.7 and Figure 2.8. The infrared spectrum of [EMIM][EtSO$_4$] at room temperature has previously been measured and calculated from density functional theory simulations [52]. This simulation allows the peaks in the infrared spectrum to be assigned to specific vibrational modes present in [EMIM][EtSO$_4$].

Since peaks in an IR spectrum represent vibrational modes of the sample molecule, the area under the IR spectrum curve should be conserved for samples with a constant number of molecules present. As the sample is heated, molecules will begin to populate higher energy levels, leading to a decrease in the peak height associated with the ground state and an increase in peak width [68]. Figure 2.6 shows the integrated areas under the “fingerprint region” (500-2000 cm$^{-1}$) and the CH stretch region of the [EMIM][EtSO$_4$] spectrum. The integrated area is reasonably well conserved for temperatures below 100 °C, however the
area begins to deviate at 100 °C. This result is in agreement with previous investigations that determined that [EMIM][EtSO₄] begins to degrade on the timescale of hours at temperatures approaching 100 °C [47]. Some of the notable peaks in the infrared spectrum are listed in Table 2.2.

![Graph showing normalized integrals of the 500-2000 cm⁻¹ and 2600-3400 cm⁻¹ spectral regions.](image)

**Figure 2.6:** Normalized integrals of the 500-2000 cm⁻¹ and 2600-3400 cm⁻¹ spectral regions. Areas have been normalized to 25 °C. Error bars are 2σ integrated over the spectral range, divided by the total area of the spectral range. The area appears to be conserved at temperatures below 100 °C, suggesting that degradation becomes noticeable between 75 and 100 °C. The area is less conserved for the spectral region containing the peaks associated with the S-O bonds of the anion.

### 2.5 Breakdown of ionic liquids

For applications where an RTIL is subjected to elevated temperatures, such as an electrochemical device under heavy load, biomass processing, or industrial separation processes, the thermal stability of the RTIL determines the upper limit of the process temperature. There-
fore significant research has been focused on determining the resistance of various RTILs to thermal breakdown [47–51]. Most of this work has focused on applying thermogravimetric techniques to determine the breakdown temperature of the RTIL. Typically, a sample mass is measured while the sample temperature is ramped linearly, and the onset of significant mass loss from the sample is designated as the breakdown temperature. Quantitative IR spectroscopy provides additional insight into the breakdown process by enabling measurement of the change in sample species concentration and also visualizing which bonds are involved in the breakdown process.

An experiment was carried out to investigate the thermal breakdown of [EMIM][EtSO₄]. A neat sample was prepared in a KBr cell and heated from 25 °C to 200 °C before being returned to 25 °C. Figure 2.9 shows the spectrum before and after heating. Significant
Table 2.2: Peaks and their associated bonds. All peak assignments are from Dhumal et al. [52] unless noted otherwise. Peaks associated with the sulfate group of the anion decrease over time in a sample held at constant temperature, suggesting that the anion is undergoing decomposition. *The 3434 cm$^{-1}$ peak appeared too slowly for a rate to be calculated from the present dataset. Peak assignment is from Zhang et al. [54].

<table>
<thead>
<tr>
<th>Peaks Decreasing</th>
<th>Bond</th>
<th>Apparent Rate at 100 °C (mol · L$^{-1}$ · min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>566</td>
<td>$O_{21}$-$S_{20}$-$O_{23}$ wag</td>
<td>-1.81E-2</td>
</tr>
<tr>
<td>578</td>
<td>$O_{21}$-$S_{20}$-$O_{23}$ wag</td>
<td>-1.81E-2</td>
</tr>
<tr>
<td>731</td>
<td>$S_{20}$-$O_{24}$ stretch</td>
<td>-1.52E-2</td>
</tr>
<tr>
<td>916</td>
<td>$O_{21}$-$S_{20}$-$O_{22}$ symmetric stretch</td>
<td>-2.29E-2</td>
</tr>
<tr>
<td>1225</td>
<td>$S_{20}$-$O_{23}$ stretch</td>
<td>-1.87E-2</td>
</tr>
<tr>
<td>1246</td>
<td>$N_{1}$-$C_{2}$-$H_{9}$+$S_{20}$-$O_{23}$ stretch</td>
<td>-1.81E-2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peaks Increasing</th>
<th>Bond</th>
<th>Apparent Rate at 100 °C (mol · L$^{-1}$ · min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>617</td>
<td>$N_{1}$-$C_{7}$ stretch</td>
<td>1.27E-2</td>
</tr>
<tr>
<td>1109</td>
<td>$H_{29}$-$C_{26}$-$H_{30}$ twist</td>
<td>2.36E-2</td>
</tr>
<tr>
<td>3434</td>
<td>OH Stretches</td>
<td>_*</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peaks Shifting</th>
<th>Bond</th>
<th>Shift (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>649</td>
<td>CN oscillation</td>
<td>649$\rightarrow$647</td>
</tr>
<tr>
<td>1061</td>
<td>$O_{24}$-$C_{25}$ stretch</td>
<td>1061$\rightarrow$1048</td>
</tr>
<tr>
<td>3103</td>
<td>$C_{2}$-$H_{9}$ stretch</td>
<td>3103$\rightarrow$3068</td>
</tr>
<tr>
<td>3151</td>
<td>$C_{2}$-$H_{9}$ stretch</td>
<td>3151$\rightarrow$3141</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Constant Peaks</th>
<th>Bond</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2982</td>
<td>$H_{13}$-$C_{6}$-$H_{14}$ symmetric stretch</td>
<td></td>
</tr>
</tbody>
</table>


changes are visible in the IR spectrum. Most notably, peaks associated with the sulfate group of the anion at 565, 578, 916, 1225, and 1246 cm\(^{-1}\) have greatly decreased in intensity. These spectral changes are consistent with decomposition of the anion, which has been shown to be the component of \([\text{EMIM}][\text{EtSO}_4]\) most susceptible to thermal degradation [71]. Furthermore, a broad peak at 3434 cm\(^{-1}\) is indicative of the presence of OH bonds [54]. These bonds may be present in a decomposition product of \([\text{EMIM}][\text{EtSO}_4]\). While the specific decomposition product could not be readily identified, the presence of an O-H stretch peak suggests that the decomposition product of the anion is an alcohol. Alcohols would be formed by the replacement of the sulfate group with a hydroxyl group on the anion.

One of the key advantages of quantitative spectral data is the ability to measure species concentrations in a sample. These quantitative measurements may be applied to IR spectra
Figure 2.9: IR spectra of [EMIM][EtSO₄] before and after heating to 200 °C. The total time the sample was held at temperatures in excess of 100 °C was approximately 1 hour. Significant decomposition has occurred. Peak associated with the SO bonds in the anion have diminished in magnitude.

A sample of neat [EMIM][EtSO₄] was prepared in a KBr cell. The sample was heated to 200 °C in 25 °C increments, with a 5 minute settling time at each temperature. Spectra were collected using an 8 scan average to reduce the acquisition time at each temperature to approximately 30 s. The resulting spectra are shown in Figure 2.10. The two peaks associated with the S₂₀−O₂₃ bond display a sigmoidal decrease with increasing temperature. The decrease in intensity is approximately linear up to 75 °C, the rate of change above 100 °C increased, and the spectrum did not recover after cooling, suggesting that thermal decomposition began occurring at a noticeable rate between 75 and 100 °C. This result is in agreement with previous thermogravimetric investigations of the thermal stability of
Figure 2.10: Detail of the most intense peaks associated with the \text{S}_{20}-\text{O}_{23} bond from 25 to 200 °C in 25 °C increments. The locations of the peaks are marked with arrows. Inset: The intensity of the \text{S}_{20}-\text{O}_{23} peaks display a sigmoidal relationship with temperature over the larger temperature range. The small narrow peaks which appear in the highest temperature data are due to changes in the amount of atmospheric water vapor present in the sample compartment between when the baseline was collected and when the sample spectrum was collected.

In order to investigate the rate of the observed degradation, a second experiment with an isothermal sample was performed. A sample of neat [EMIM][EtSO_4] was prepared in a KBr cell. The sample was heated to 100 °C and the heated cell was allowed to equilibrate for 5 minutes. Spectra were then collected every five minutes using an 8 scan average. These spectra were then used to calculate the concentration of [EMIM][EtSO_4], using the 1225 and 1246 cm\(^{-1}\) peaks associated with the SO stretch of the sulfate group on the anion. Figure 2.11 shows the concentration of the sample over time. Over the course of the test,
the peaks associated with the sulfate group decrease, suggesting that the anion is being degraded. Over the 25 minute duration of the test, the calculated sample concentration drop by approximately 9%, or 0.02 mol·L⁻¹·min⁻¹. This rate of degradation is greater than the mass loss measured by isothermal thermogravimetric methods which show that [EMIM][EtSO₄] undergoes mass loss at 100 °C [47]. Fernandez et. al. measured a mass loss of about 1% over 25 min. at both 80 and 120 °C. Here, the heights of the SO bonds indicate a loss of about 9% of the starting concentration, suggesting that degradation occurs more rapidly than thermogravimetric techniques measure. However, this spectroscopic method does not rely on the volatilization of decomposition products to detect the thermal breakdown of the ionic liquid. The peaks at 1225 and 1246 cm⁻¹ may present a powerful tool to detect degradation of [EMIM][EtSO₄] and monitor the health of the ionic liquid in future experiments.

Spectroscopic methods applied to heated samples allow for in-situ investigations of the fundamental structures, solvation properties, and breakdown characteristics of RTILs. The quantitative spectra presented in this work also allow for non-invasive in-situ and in-operando diagnostics of species concentration and temperature for future applications of [EMIM][EtSO₄], such as electrochemical devices or chemical processes. In Chapter 3, quantitative absorption spectra are applied to develop an optical sensor for monitoring the purity of the ionic liquid [EMIM][TFSI] for control of the industrial synthesis process. In Chapter 4, quantitative absorption spectra are applied to allow in-operando measurements of species concentrations in a Na-Cu-I⁻ battery.
Figure 2.11: The 1225 and 1246 cm\(^{-1}\) peaks associated with the SO stretch of the anion. Inset: The concentration of SO bond present in an isothermal sample at 100 °C over time, calculated from the observed peak heights. The small narrow peaks which appear in the last data are due to changes in the amount of atmospheric water vapor present in the sample compartment between when the baseline was collected and when the sample spectrum was collected.
CHAPTER 3
OPTICAL DETECTION OF IMPURITES IN IONIC LIQUIDS FOR INDUSTRIAL PRODUCTION

An accurate measurement of $\epsilon(\nu)$ allows measurement of species concentrations, temperature, or other parameters from the light absorbed by a sample. If quantitative spectra are available for the components of a mixture, the components of the mixture may be identified and their concentrations measured. Here, previously measured quantitative UV-vis spectra of the ionic liquid 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) and methylimidazolium (MIM), a precursor of [EMIM][TFSI] that may be present as an impurity in the finished ionic liquid, are used to develop an optical sensor for detecting the presence of MIM in [EMIM][TFSI] [56].

The favorable properties of RTILs such as their low vapor pressure [31, 32, 42, 72], their stability across a wide range of temperatures, and their wide electrochemical windows [73–75] have the potential to create a large industrial market for RTILs. To supply industrial demands for RTILs, a cost effective synthesis process for mass production is needed. However, the properties of RTILs are highly dependent on purity. For example, the electrochemical window of [EMIM][TFSI] has been shown to be dependent on the water content of the sample [75, 76]. Residual precursors and byproducts of RTIL synthesis can lead to electrode corrosion and other performance degradation mechanisms. For example, synthesis of the [EMIM]-cation typically begins with MIM, whose redox stability limit is within the electrochemical window of [EMIM][TFSI]. Currently, most RTILs are produced through batch processes. After the synthesis reaction is complete, the product must be separated from impurities, adding to the cost of RTILs. Due to the low vapor pressure of ionic liquids, purification through a distillation process is not feasible, and considerable effort is spent in purifying ionic liquids through filtration or recrystallization processes [70, 77].
Continuous flow synthesis processes have recently been developed that have the potential to significantly reduce costs – making more industrial RTIL applications feasible [77, 78]. In a continuous flow process, it is desirable to monitor the purity of the finished product in real time as the product exits the production line to ensure product quality and process control. Synthesis of quaternary amine cations pose particular challenges due to the exothermic reaction and requirement that the precursors’ stoichiometry be precisely controlled. Any deviation from a 1:1 stoichiometry of tertiary amine and quaternizing agent will result in an excess of one reactant that may be difficult to remove from the product RTIL. By monitoring the purity of the finished product, it is possible to determine if the synthesis process is proceeding within normal operating conditions [77, 78]. Currently, methods for determining the purity of RTILs such as ion chromatography tend to be expensive and ex-situ [79, 80]. An in-situ sensor which is capable of determining the purity of the RTIL in real time would allow the production process to be self monitoring.

The ultraviolet absorption spectrum provides a unique identifier for ionic liquids and their chemical precursors. Previously, it was shown that by using UV spectroscopy, it was possible to detect the presence of impurities in ionic liquids by analyzing the absorption spectrum of each constituent [55]. The aim of the work reported here is to apply these findings to the problem of sensing impurities in real time. The time response and non-intrusive nature of optical sensors make them ideal for monitoring chemical processes. For example, optical sensors are commonly used to measure the presence of analytes in samples [81–83]. Although spectroscopic methods have been used before to characterize RTILs [84], to the best of the authors’ knowledge the sensor presented in this chapter is the first spectroscopic device designed for process control in the production of RTILs.

3.1 The sensing mechanism

As we discussed in Chapter 1, the molar absorption coefficients of species add linearly in many cases. This lead us to the Beer-Lambert law for mixtures (Equation 1.24)
\[-\ln \left( \frac{I}{I_0} \right) = \sum_{i=1}^{n} \epsilon_i c_i L \]  
(3.1)

In this case, the absorbance at any given point in the spectrum will be a function of the cell pathlength and concentration of [EMIM][TFSI] and MIM in the sample.

\[-\ln \left( \frac{I}{I_0} \right) = \alpha = (\epsilon_{\text{TFSI}} c_{\text{TFSI}} + \epsilon_{\text{MIM}} c_{\text{MIM}}) L \]  
(3.2)

Since both \( \epsilon_{\text{TFSI}} \) and \( \epsilon_{\text{MIM}} \) are constant material properties and the pathlength \( L \) is fixed, the absorbance \( \alpha \) depends on the concentrations \( c_{\text{TFSI}} \) and \( c_{\text{MIM}} \). If a wavelength where \( \epsilon_{\text{TFSI}} \) and \( \epsilon_{\text{MIM}} \) are different from each other is selected, \( \alpha \) will vary as a function of \( c_{\text{TFSI}} \) and \( c_{\text{MIM}} \).

Figure 3.1 shows the measured UV absorption spectra of [EMIM][TFSI] and MIM at ambient conditions. From these spectra, it can be seen that MIM has an absorption peak near 275 nm, while [EMIM][TFSI] has an absorption peak near 265 nm. Between 275 nm and 300 nm, the absorption cross-section of MIM is greater than that of [EMIM][TFSI]. At wavelengths longer than 340 nm, neither MIM nor [EMIM][TFSI] absorb light. The sensor described in this work utilizes these spectral properties to determine the presence of MIM in [EMIM][TFSI].

Due to the differences in spectral properties between MIM and [EMIM][TFSI] seen in Figure 3.1, the presence of MIM may be detected in a sample by changes in absorption at wavelengths between 275 nm to 300 nm. In order to measure the differences in absorption between [EMIM][TFSI] and MIM, a custom LED array with wavelengths selected to measure the spectral features of [EMIM][TFSI] and MIM was obtained from Sensor Electronic Technologies Inc. A diagram of the array may be seen in Figure 3.2.

### 3.2 Sensor construction and testing

The LED array contained 9 separate diodes: 4 diodes which emitted at a peak wavelength of 295 nm (9.7 nm full-width half-maximum), 4 diodes which emitted at a peak wavelength of 320 nm (10.4 nm full-width half-maximum), and as a single 365 nm diode (18.1 nm full-
Figure 3.1: Absorption spectra of [EMIM][TFSI] and MIM. The full-width half-maximum range of the 295 nm LED channel is shown as the shaded area on the left. The shaded area on the right is the full-width half-maximum of the 365 nm channel. Data were previously collected and presented as described in [55].

The LED array was housed in a 12 pin TO-8 package. This package was soldered to a custom printed circuit board which was designed to fit into a standard 1 in. optical mount. The LED was driven by a 0-12 V logic circuit with appropriate current limiting resistors to protect the diodes in the array. The 295 nm diodes were used to detect increased absorbance due to the presence of MIM. While a larger difference in absorbance is seen at about 270 nm, inexpensive diodes at this wavelength are not yet commercially available. The 365 nm diode has been selected to provide a reference for the transmission through the RTIL. The 320 nm diodes are used for detecting a second impurity which is specific to the proprietary synthesis process developed by Coorstek Flourochemicals.
Figure 3.2: The optical layout of the sensor. Two detectors are used to measure both the output of the LED (bottom) and the light transmitted through the RTIL (right). The beam is split using an uncoated UV fused silica window to allow the reference detector (bottom) to measure LED output. The RTIL flows through an optical flow cell manufactured by Flow Injection Labs. Free space optics are used to focus the light through the cell and onto the detector. Not to scale.
The RTIL flowed through a 2.5 mm path length flow cell (FIA Labs SMA-Z-2.5 #79048) constructed from PEEK and fitted with a pair of fused silica windows to allow transmission of ultraviolet light. Light was focused through the cell’s windows by means of a series of free space optics mounted on ThorLab’s 30 mm cage mount components, as shown in Figure 3.2. The light transmitted through the RTIL was measured by a ThorLabs PDA10A amplified photodetector (measurement detector). An uncoated UV fused silica window directed a portion of the LED light to a second PDA10A to monitor the output of the LED (reference detector). The purpose of the reference detector was to measure and correct for variation in the output intensity of the LED. Detector output signals were filtered with 50 Hz RC low pass filters (R=330 Ω, C=10 µF) and read by a National Instruments PCI-MIO-16E-1 data acquisition card.

[EMIM][TFSI] (trade name Iolyte P1) was obtained from Coorstek Flourochemicals. Total halide content was less than 100 ppm and water content was less than 20 ppm. The [EMIM][TFSI] was used without further purification. MIM was also obtained from Coorstek Flourochemicals. All samples were stored and prepared in a dry nitrogen environment. Samples of [EMIM][TFSI] with known MIM concentrations were created in a controlled atmosphere glovebox with low oxygen and low humidity. Quantities of MIM were weighed using a digital balance and added to samples of pure [EMIM][TFSI]. Separate 2 mL samples were prepared in syringes and injected through the flow cell while sensor readings were recorded. Each sample was discarded after passing through the sensor to prevent contamination. Only steady-state readings were retained to avoid erroneous readings due to mixing of samples in the flow cell.

3.3 Determination of MIM concentration

Accurate MIM concentration measurements require correcting for background noise, fluctuation is LED output, and for changes in optical transmission through the cell. Background subtraction removes the small DC offset due to ambient light striking the detectors. This is accomplished by subtracting the voltage reading from each detector when all LED wave-
lengths are off. Fluctuations in the intensity of the LED are removed by taking the ratio of the measurement detector signal, $I_M$, over the reference detector signal, $I_R$: $I_M/I_R$. Taking this ratio in real-time corrects for transient fluctuations in LED output as well as intensity drift over time. These corrections can be represented in the Beer-Lambert law (Equation 1.22) as:

$$\ln \left( \frac{I_{M}^{295} I_{0,R}^{295}}{I_{0,M}^{295} I_{R}^{295}} \right) = \epsilon^{295} X_{MIM} c L$$

(3.3)

where $I_0$ denotes the measurement in a pure [EMIM][TFSI] sample, and the superscript denotes the wavelength of the LED that was active while the voltage reading was taken. $X_{MIM}$ is the mole fraction of MIM present in the sample, and $c$ is the total molar concentration of the mixture. Each value of $I$ was calculated by averaging the voltage reading while that wavelength was on (as shown by the shading in Figure 3.3).

Monitoring the light transmitted through the RTIL at 365 nm corrects for beam steering, optical scattering from small bubbles in the sample, and variability in the overall absorbance of the RTIL (as has been reported even for high purity samples [70, 85, 86]). The light lost due to these factors is modeled with a modified version of the Beer-Lambert law:

$$\ln \left( \frac{I_{M}^{365} I_{0,R}^{365}}{I_{0,M}^{365} I_{R}^{365}} \right) = \epsilon^{365} X_{MIM} c L + \tau$$

(3.4)

where $\tau$ is attenuation not due to the presence of MIM. Taking this ratio for the 365 nm signal results in a direct measurement of signal attenuation not due to absorption. This is possible because the absorption cross-section of MIM at 365 nm ($\epsilon^{365}$) is zero.

$$\ln \left( \frac{I_{M}^{365} I_{0,R}^{365}}{I_{0,M}^{365} I_{R}^{365}} \right) = \epsilon^{365} X_{MIM} c L + \tau = \tau$$

(3.5)

In order to correct for this extra attenuation, the signal ratio for the 365 nm channel is subtracted from the 295 nm signal ratio. Using the properties of logarithms, the 365 nm channel may be subtracted from the 295 nm channel to eliminate the $\tau$ term and produce a final corrected ‘absorbance ratio’:
Figure 3.3: Raw voltage readings from the measurement detector. Each wavelength of the LED array is seen as a discrete pulse in the voltage reading. \( I \) values are taken by averaging the ‘top hat’, shown in blue, of each voltage pulse. The 320 nm channel is for detecting an impurity which is proprietary to the Coorstek Fluorochemicals synthesis process and is not discussed here. The standard deviation of points in the ‘top hat’ is also recorded to allow uncertainty in the measured concentration of MIM to be calculated.

\[
- \ln \left( \frac{I_{295}^M I_{365}^R I_{365}^{0,M} I_{365}^{0,R}}{I_{295}^{0,M} I_{295}^{0,R}} \right) = \left( \epsilon_{295} X_{\text{MIM}} c L + \tau \right) - \tau \quad \text{(3.6)}
\]

\[
= \epsilon_{295} X_{\text{MIM}} c L \quad \text{(3.7)}
\]

Over a small range of MIM concentrations, \( c \) may be assumed to be constant. Thus the corrected absorbance ratio provides a direct measure of the MIM mole fraction in the RTIL if the flow cell path length, \( L \), and the MIM absorption cross-section, \( \sigma_{295} \), are known.
Figure 3.4: Sensor results for MIM in [EMIM][TFSI]. Error bars are calculated through a propagation of uncertainties based on the standard deviation of voltage readings for each wavelength. Additionally, the absorbance ratio has been calculated from the spectra in Figure 3.1 (solid line). The absorbance ratio is defined in Equation 3.7.

3.4 Results

Figure 3.4 shows the two color sensor’s response to MIM in [EMIM][TFSI]. As predicted by the results shown in Figure 3.1, the absorbance ratio (Equation 3.7) increases with increasing MIM content due to increased absorption of the 295 nm light. The absorbance ratio has also been predicted from the spectra shown in Figure 3.1 by calculating an average absorbance across the spectral range of the 295 nm and 365 nm channels of the LED array. The average absorbance was calculated by performing a numerical integration of the molar absorptivity of both MIM and [EMIM][TFSI] over the spectral range of the 295 nm and 365 nm channels of the LED. This integrated average molar absorption coefficient was then
multiplied by the MIM mole fraction and cell path length for comparison with the sensor absorbance ratio (Equation 1.22). This comparison is complicated by the fact that the intensity of the LEDs was not a constant with respect to wavelength. The integration of the molar absorptivity was therefore weighted according to the output of the LED. For the integration, the output of the LED was assumed to be spectrally Gaussian and each peak was integrated from two standard deviations below the peak output wavelength to two standard deviations above peak output. Thus the spectral average of the absorption cross-section becomes:

$$\bar{\varepsilon} = \left( \frac{C}{\lambda_f - \lambda_0} \right) \int_{\lambda_0}^{\lambda_f} \Omega(\lambda) \varepsilon(\lambda) d\lambda$$

(3.8)

where $\bar{\varepsilon}$ is the average molar absorptivity over the wavelength range of the LED, $C$ is a constant which takes into account the difference in the LED intensity and detector responsivity for each LED channel (For the 295 nm channel $C = 0.25$, for 365 nm $C = 8.5$), $\Omega$ is the Gaussian weighting function to estimate the spectral dependence of the LED’s output, $\lambda_0$ is the wavelength two standard deviations shorter than the peak output wavelength of the LED, and $\lambda_f$ is the wavelength two standard deviations longer than the peak output wavelength.

The limit of detection (LOD) of the sensor was calculated from the standard deviation of 82 sensor readings of pure and low MIM concentration (5 w%) samples, as described by Loock and Wentzell [87]. The 99% confidence LOD was determined to be 4 molar percent MIM. The sensor described in this article is less sensitive than methods such as gas chromatography-mass spectrometry which is used to measure ppm levels of MIM in [EMIM][TFSI]. However, the 4 molar percent LOD is sufficient to determine if the continuous flow synthesis process is operating outside of normal parameters.

The uncertainty of each measurement in Figure 3.4 is calculated through a propagation of uncertainties based on the standard deviation of all the voltage readings used in the measurement. By reducing the noise further through the use of a lock-in amplifier or another filtering scheme, the LOD of the sensor could be reduced.
CHAPTER 4
IN OPERANDO OPTICAL SPECTROSCOPY MEASUREMENTS OF A SODIUM-COPPER-IODIDE CELL

An electrochemical battery stores electrical energy through an electrochemical reaction which converts the electrical energy into chemical potential energy. The chemical reaction takes place in two half cell reactions at each of the electrode interfaces. At one electrode, reactants are reduced by combining with electrons.

\[ aA + ne^- \longleftrightarrow cC \quad (4.1) \]

where A and C are chemical species participating in the half cell reaction. a and c are the stoichiometric coefficients and n is the number of electrons involved in the reaction.

At the opposite electrode, reactants are oxidized. This process liberates electrons.

\[ bB \leftrightarrow dD + ne^- \quad (4.2) \]

where B and D are the species participating in the reaction. b and d are the stoichiometric coefficients, and n is the number of electrons participating in the reaction.

By combining the two half cell reactions, the overall electrochemical reaction can be balanced.

\[ aA + bB \leftrightarrow cC + dD \quad (4.3) \]

The basic unit of a battery is the cell, which is comprised of three parts.

- **The cathode:** The electrode where species are oxidized during cell discharge. Electrons enter the battery from the external circuit and are combined with cations at the cathode during cell discharge.

- **The anode:** At the anode, species are reduced during cell discharge. The reduction reaction liberates electrons which then enter the external circuit to do work.
**The electrolyte:** The electrolyte is an electrically insulating, ion-conducting material that allows ions to migrate between the two electrodes. The electrolyte must be electrically insulating to force electrons from the electrochemical reaction through the external circuit to do work.

Figure 4.1 shows the basic parts of a cell. Important cell properties such as the voltage and maximum current density of the cell are determined in large part by the overall cell reaction.

![Figure 4.1: The basic components of a cell.](image)

In any electrochemical cell, the thermodynamics of the overall cell reaction determine the maximum cell potential. As current is drawn from the cell, the cell voltage will begin to
drop due to internal cell losses and inefficiencies. The maximum theoretical cell voltage is therefore called the **open circuit voltage (OCV)** [88].

The open circuit voltage of a cell is determined entirely by the thermodynamics of the overall cell reaction. For a chemical reaction, the work which may be extracted from that reaction is given by the change in Gibbs free energy between the reactants and products. The following explanation of the relationship between the open circuit voltage of a cell and the thermodynamics follows from *Fuel Cell Fundamentals* [88].

The Gibbs free energy is defined in thermodynamics as:

\[
G = U + PV - TS
\]  

(4.4)

where \( G \) is the Gibbs free energy, \( U \) is the total system energy, \( P \) is the pressure of the system, \( V \) is the volume of the system, \( T \) is the temperature of the system, and \( S \) is the entropy of the system. Taking the derivative, the change in Gibbs free energy when the system moves from one state to another is therefore:

\[
dG = dU - TdS - SdT + PdV + VdP
\]  

(4.5)

The \( dU \) term may be expanded to express work done by the system and the resulting change in entropy of the system. Furthermore, since we are examining an electrochemical system, the work term may be split into mechanical and electrical work performed by the system.

\[
dG = TdS - dW - TdS - SdT + PdV + VdP
\]  

(4.6)

\[
dG = -(PdV_r + dW_{elec}) - SdT + PdV_r + VdP
\]  

(4.7)

\[
dG = -dW_{elec} - SdT + VdP
\]  

(4.8)

If we assume the cell reaction takes place under standard temperature and pressure (STP) conditions at a constant temperature \((dT = 0)\) and a constant pressure \((dP = 0)\) process, the change in Gibbs free energy becomes:

\[
dG = -dW_{elec}
\]  

(4.9)
Now that we have shown that the work available in the chemical reaction is determined by the change in Gibbs free energy of the reaction, we must relate the change in Gibbs free energy to the cell voltage. Electrical work is defined as:

\[ W_{\text{elec}} = EQ \] (4.10)

where \( E \) is a potential difference measured in volts and \( Q \) is the amount of charge that passes through the potential. In an electrochemical reaction, the charge \( Q \) will be carried by electrons. In order to easily measure the amount of electrons passing through the cell, it is convenient to introduce a new constant.

\[ Q = nF \] (4.11)

In Equation 4.11, \( n \) is the number of moles of electrons which pass through the potential difference \( E \), and \( F \) is Faraday’s Constant, which is 96,487 C/mol. \( N \) is the number of moles of reaction that have occurred to transfer charge \( Q \). Faraday’s constant allows us to easily translate between electrical measurements of current and charge and the moles of reactants consumed by the reaction, as well as the amount of products produced by the reaction.

By substituting Equation 4.9 into Equation 4.10, we now have the relationship between cell voltage and the change in Gibbs free energy associated with the electrochemical reaction.

\[ \Delta G_{\text{rxn}} = -nFE \] (4.12)

Since we assumed the reaction takes place at standard conditions (\( T=25 \, ^\circ\text{C}, P=1 \, \text{atm} \)), Equation 4.12 is often expressed as:

\[ E^0 = -\frac{\Delta G_{\text{rxn}}^0}{nF} \] (4.13)

where \( E^0 \) is known as the standard-state reversible voltage and \( \Delta G_{\text{rxn}}^0 \) is the standard-state free energy change associated with the electrochemical reaction. \( E^0 \) is the open cell voltage of a cell which operates entirely at STP conditions. However, most cells do not operate at exclusively STP conditions. The effects of temperature, pressure, and species chemical potential can be taken into account to calculate the open circuit voltage for any cell.
In order to account for the effect of temperature on the open circuit voltage, the original assumption of constant temperature operation in Equation 4.9 must be changed. We take the derivative of the Gibbs free energy with respect to temperature at constant pressure.

\[
\frac{d}{dT}(dG)_P = -dW_{\text{elec}} - SdT + PdV
\]  

(4.14)

\[
\frac{dG}{dT}_P = -S
\]  

(4.15)

We have already related the Gibbs free energy to the cell potential. If we combine Equations 4.15 and 4.13, we will arrive at an expression for the change in cell voltage with respect to temperature.

\[
\frac{dE}{dT}_P = \frac{d}{dT} \left( \frac{-G}{nF} \right)_P = \frac{\Delta S}{nF}
\]  

(4.16)

The cell voltage at any temperature is therefore the cell voltage at STP plus the change in cell voltage due to the effects of temperature. If we assume that \(\Delta S\) is constant with temperature and integrate Equation 4.16 from \(T_0\) to \(T\), then the expression for the reversible cell potential at a given temperature \(T\) is:

\[
E_T = E^0 + \frac{\Delta S}{nF}(T - T_0)
\]  

(4.17)

In order to arrive at Equation 4.17, we have assumed that the change in entropy per unit temperature \(\Delta S\) is a constant. For most engineering applications, this assumption provides acceptable accuracy. If higher accuracy is desired, \(\Delta S\) may be integrated over the temperature range.

To account for variations in the reversible cell potential due to differences in reactant and product concentrations as well as pressure, the variation of the Gibbs free energy with species concentration is examined. The variation of the Gibbs free energy with concentration is given by:

\[
\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq i}
\]  

(4.18)
where $\mu_i$ is the chemical potential of species $i$. The chemical potential describes the change in a system’s free energy when the number of molecules of species $i$ changes. Chemical potential is not easily measured directly. To relate the chemical potential to more convenient measurable units the activity of the chemical species is used.

$$
\mu_i = \mu_i^0 + RT \ln a_i \quad (4.19)
$$

In Equation 4.19, $a_i$ is the activity of species $i$. The activity determines the difference between the chemical potential at standard conditions, $\mu_i^0$, and non-standard conditions. Relating this change in chemical potential to the change in Gibbs free energy yields:

$$
dG = \sum_{i=1}^{N} \mu_i dn_i = \sum_{i=1}^{N} \left( \mu_i^0 + RT \ln a_i \right) dn_i \quad (4.20)
$$

where $N$ is the total number of species involved in the cell reaction. When we examine the change in Gibbs free energy between the products and reactants of the generic electrochemical reaction in Equation 4.3, we are able to determine the total change in Gibbs free energy due to the reaction.

$$
\Delta G = \Delta G_0 + RT \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right) \quad (4.21)
$$

Finally, Equation 4.21 may be combined with the relation $\Delta G = -nFE$ to determine the change in cell voltage with respect to species activity.

$$
E = E^0 - \frac{RT}{nF} \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right) \quad (4.22)
$$

For any reaction with an arbitrary number of products and reactants, Equation 4.22 becomes:

$$
E = E^0 - \frac{RT}{nF} \ln \left( \frac{\prod a_{\text{products}}^{\nu_i}}{\prod a_{\text{reactants}}^{\nu_i}} \right) \quad (4.23)
$$

where the exponents $\nu_i$ are the stoichiometric coefficients for each species. Equation 4.23 is known as the Nernst equation. The Nernst equation describes the cell voltage as a function of species activities. Since the Nernst equation uses species activities and activity is a function of pressure and concentration, the Nernst equation accounts for cell voltage differences due to varying pressure and concentration.
The Nernst equation does not fully account for the variation of cell potential with temperature. To incorporate the effects of temperature on the cell potential, we can substitute Equation 4.17 into the Nernst equation.

\[
E = E^0 + \frac{\Delta S}{nF}(T - T_0) - \frac{RT}{nF} \ln \left( \frac{\prod a_{\text{products}}^{\nu_i}}{\prod a_{\text{reactants}}^{\nu_i}} \right) \tag{4.24}
\]

### 4.1 Real batteries: Polarization losses

Equation 4.24 can be used to determine the maximum theoretical voltage a given cell chemistry will produce. However, real batteries never achieve this theoretical voltage due to internal losses and inefficiencies. In order to understand the behavior of a real cell, it is necessary to examine the causes of the voltage losses. Discussion of the voltage losses is summarized from *Linden’s Handbook of Batteries* [89]. These voltage losses are known as **polarization losses**, and fall into three categories.

- **Ohmic losses**: During cell operation, electrochemical ion species must move through the cell electrolyte from one electrode to the other. Since real electrolytes are not perfectly ion conducting, the ions are subject to some resistance. These losses follow Ohm’s Law, \( V = IR \) where \( I \) is the ionic current in the cell and \( R \) is the resistance of the electrolyte to to ionic current.

- **Activation polarization**: Chemical reactions do not occur instantaneously at the anode and cathode. Slower reaction kinetics lower the cell potential. Near the charged surface of the electrode in a liquid electrolyte, polar electrolyte molecules may arrange themselves into an electrical double layer. This double layer of electrolyte molecules slows the adsorption of electrochemical species onto the electrode, further slowing the reaction.

- **Concentration polarization**: Under high current draws, the cell operation begins to be limited by mass transport within the cell. Electrochemical reactions take place at the electrode surfaces in the cell. At sufficiently high current densities, the rate of diffusion
of reactants to the electrode and products away from the electrode will be unable to sustain the current being drawn from the cell. The cell potential will drop rapidly.

These polarization losses are illustrated in Figure 4.2. The real cell potential is then the theoretical open circuit potential less the losses due to ohmic, activation, and concentration polarization. Polarization losses are dependent on the current flowing through a cell. However, two batteries with the same chemistry but different physical sizes will behave differently when subjected to the same current draw. It is therefore convenient to define polarization losses in terms of **current density**, or current per unit area. Calculations in terms of current density allow us to compare batteries with different geometric designs.

![Figure 4.2: Polarization losses in a real cell. The real cell potential is the theoretical (thermodynamic) cell voltage less the ohmic, activation, and concentration polarization losses.](image)

\[
E = E_{OCV} - \eta_{act,c} - \eta_{conc,c} - \eta_{act,a} - \eta_{conc,a} - iR 
\]  

(4.25)

In Equation 4.25, \(E_{OCV}\) is the theoretical open circuit potential calculated from Equation 4.24. The activation losses of the cell are represented by \(\eta_{act,c}\) and \(\eta_{act,a}\), where the subscripts \(a\) and \(c\) represent the anode and cathode respectively. \(\eta_{conc,c}\) and \(\eta_{conc,a}\) represent the concentration losses in the cell. The activation and concentration polarization losses
have been split into two terms because the kinetics and transport processes at each electrode may be different. Finally, the term $iR$ represents the ohmic losses due to the diffusion of ions through the cell electrolyte.

We have discussed how the cell voltage of a battery is dependent on the current density being drawn from the cell. The cell voltage of a battery also varies as the battery is discharged. Figure 4.3 shows different discharge curves for batteries.

![Discharge curves for various batteries](image)

**Figure 4.3**: Discharge curves for various batteries. The ideal battery maintains its cell voltage through the entire discharge. Curve 1 shows a cell with a relatively low internal resistance. Curve 2 shows a cell with a higher internal resistance, or a cell being discharged at a higher rate.

In Figure 4.3, the ideal battery maintains a constant voltage equal to the theoretical cell voltage until the cell is completely expended. Due to the polarization losses discussed earlier, any real cell will not achieve the ideal discharge curve. Curve 1 shows a more realistic cell discharge curve. The cell potential never reaches zero and not all the stored energy in the cell is released. Curve 2 shows a poorly performing cell. The voltage drops rapidly and much of the stored energy cannot be recovered. The constantly changing cell potential would make voltage regulation difficult for any device using battery 2.
New battery chemistries are typically tested by means of electrochemical measurements. Electrochemical measurements apply different voltage or current conditions to a cell under test and measure the cell’s response to stimuli [89, 90].

4.2 Galvanostatic charge-discharge cycling

The most common form of battery testing is constant current, or galvanostatic charge-discharge cycling. In this testing regime, a constant current is applied to charge the cell, and the cell voltage is monitored. The battery is discharged by applying a constant current in the opposite direction of the charging current.

As the cell is charged, the balance of electrochemical products and reactants shifts, leading to an increased cell potential. This change in potential is recorded by the galvanostat instrument. When the cell reaches a predefined fully charged voltage level, the current is reversed through the cell. The cell voltage will now drop as the electrochemical reaction returns to the original discharged state.

Information about the kinetics of the electrochemical reaction and the effectiveness of the cell design can be obtained from galvanostatic measurements. A battery with slow kinetics will exhibit a significantly lower cell potential during discharge tests at higher discharge rates. Some batteries may exhibit multiple distinct potential drops during the course of a discharge, indicating that multiple discharge mechanisms, such as intercalation or deintercalation, the insertion and removal of molecules from layered structures in the electrodes, take place during the full charge-discharge cycle [89].

4.3 Cyclic voltammetry

Cyclic voltammetry also provides a powerful tool for understanding the electrochemical reactions taking place inside a cell. Cyclic voltammetry is commonly used to investigate the activation energies and rates of electrochemical reactions in a cell [91, 92].

In a cyclic voltammetry experiment, the cell potential is varied linearly in time while the current is monitored. Figure 4.4 shows a typical voltage sweep that might be used in a cyclic
voltammetry experiment. The cell potential varied linearly from an initial potential of $E_0$ to some maximum potential $E_\lambda$. The sweep is then reversed until the cell potential is at a minimum, $-E_\lambda$. Note that $E_\lambda$ and $-E_\lambda$ do not necessarily need to be the same magnitude, but frequently are.

![Diagram of cyclic voltammetry](image)

**Figure 4.4:** In a typical cyclic voltammetry experiment, the electrode potential is swept linearly at a predefined scan rate while the cell current is measured.

The measured cell current is frequently plotted against the applied cell potential, resulting in a cyclic voltammogram. An example voltammogram is shown in Figure 4.5. In Figure 4.5, a perfectly reversible reaction is shown. The reaction is reversible because the peak cathodic and anodic currents, $i_c$ and $i_a$, are equal [93, 94]. In a reversible reaction, the electron transfer at the electrode is fast and the reaction rate is limited by the diffusion of species to the electrode [90]. The potential at which the maximum current peaks occur, number of peaks present in the voltammogram, and the variation in the shape of the voltammogram with scan rate all provide useful insights into the electrochemical processes in the cell.

However, both galvanostatic and cyclic voltammetry are only capable of measuring species which are electrochemically active. In real battery systems, electrolytes may be a complex mixture of solvents, stabilizers, and electrochemical species. Reactions may take
place in the electrolyte without electron exchanges between the species and the electrodes of the cell. These reactions are not measurable with traditional electrochemical techniques. It is also challenging to identify and measure chemistries where reactions occur in series or multiple pathways occur simultaneously.

4.4 Spectoelectrochemistry

Optical spectroscopic methods are able to provide complementary information to electrochemical measurements. Optical techniques such as UV-vis or IR absorption spectroscopy are well suited to identifying and quantifying species, even if they are not electrochemically active. Most optical techniques are also non-destructive and non-invasive, which allows the techniques to be coupled to electrochemical measurements without affecting the electrochemical measurements [90].

Optical techniques also have the ability to provide spatially resolved measurements in an electrochemical cell. One of the strengths of electrochemical techniques is the direct relationship between the charge flowing through the cell and the number of individual chemical reactions taking place in the cell (Equation 4.11). However, the cell current simply measures
the sum total of all the individual reactions taking place on the electrode surface. Any spatial information about where on the electrode surface the reactions are taking place is lost. Optical methods employing a tightly focused beam of light may be used to interrogate small areas of the electrode to study any inhomogeneities on the electrode surface.

UV-vis spectroscopy is applied here to the study of the Na-Cu-I$^-$ battery chemistry. This battery chemistry is an attractive candidate for study for three reasons. First, there are relatively few chemical species present in the cell. Second, some of the species present do not participate in the cell reaction and therefore cannot be measured with traditional device level electrochemical techniques. Finally, a published computational model is available to compare with experimental results [95].

The anode side of the cell consists of molten sodium metal. The cathode side of the cell contains a copper electrode in an aqueous solution of NaI. The two electrodes are separated by a Nasicon ion exchange membrane, which conducts sodium ions between the electrodes. Nasicon is a portmanteau of ‘sodium (Na) ion super conductor’ and describes a family of ceramic materials with very high sodium ion conductivities [96, 97]. The two half cell reactions taking place in the cell are

\[
\begin{align*}
\text{Anode :} & \quad \text{Na}^+ + e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} \text{Na} \\
\text{Cathode :} & \quad \text{Cu}(s) + 2\text{I}^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} \text{CuI}_2^{\text{(aq)}} + e^- 
\end{align*}
\]

(4.26) (4.27)

Figure 4.6 shows a schematic of the cell operation. At the cathode side of the cell, we may expect to find CuI$_2^-$, I$^-$, I$_2$, I$_3^-$, and Na$^+$ in solution. Although only I$^-$, CuI$_2^-$, and Na$^+$ are expected to participate in the electrochemical reaction, in a solution with an appreciable concentration of I$^-$ ions, there will be some equilibrium concentration of I$^-$, I$_2$, and I$_3^-$. The equilibrium concentration is a function of temperature, solution pH, and other factors.

At the cathode of the cell, I$^-$ is reduced during cell charging to form CuI at the electrode surface. In order for the CuI to be dissolved, a second I$^-$ must complex the CuI to form CuI$_2^-$.
This process is interesting because the complexation of CuI is not electrochemically active. CuI$^-$ does however absorb in the UV which allows its concentration to be measured spectroscopically.

![Schematic of cell during charging](image)

**Figure 4.6:** A schematic of the cell during charging. At the cathode, Cu combines with aqueous I$^-$ to form CuI. A second I$^-$ ion complexes the CuI, forming CuI$_2^-$ in solution.

### 4.5 Measurement of relevant absorption cross-sections

In order to make a measurement of the concentrations of CuI$_2^-$ and the other species in the cell, the absorption spectrum of each species must first be determined. From the Beer-Lambert law (Equation 1.22), a measurement of species concentration can be made by absorption spectroscopy if the pathlength and molar absorption coefficient of the species in question is known. For a mixture of species present in the cell electrolyte, if all the molar absorption coefficients are known then Equation 1.24 may be used to determine the concentration of each species.

In the Na-Cu-I$^-$ battery chemistry, measurement of the molar absorption coefficient for each species is complicated by the fact that CuI$_2^-$ is not stable in aqueous solution without the presence of I$^-$ ions [98]. As was discussed above, there will be some equilibrium concentration...
of I\(^-\), I\(_2\), and I\(_3^-\) present in the solution. It is therefore required that the molar absorption coefficient of CuI\(_2^-\) be measured in an aqueous mixture of CuI\(_2^-\), I\(^-\), I\(_2\), and I\(_3^-\).

4.6 Quantum chemical modeling of the UV-vis spectrum

Due to the difficulty of isolating CuI\(_2^-\) experimentally to measure the molar absorption coefficient, ab initio quantum chemistry methods can be used to calculate the absorption spectrum. Quantum chemical methods calculate the frequency and intensity of absorption lines from a computational model of a molecule. These calculated spectra may be used to select diagnostic techniques by identifying UV-vis, IR, and Raman peaks that may be used for measurements. For quantum ab initio simulations, methods are defined by two major parameters, the level of theory and the basis set. An in-depth discussion of how quantum chemical simulations are performed is beyond the scope of this work, but a basic explanation of the methods and their advantages is given here in the context of calculating the UV-vis absorption spectrum of CuI\(_2^-\).

The level of theory describes the amount of detail captured by a quantum physical model of the molecule. The movement of electrons and atomic nuclei in a molecule are governed by Schrödinger’s equation, which cannot be solved analytically for practical systems [99]. The Schrödinger equation takes into account the interactions between electrons and the force field created by the atomic nuclei in a molecule. The electrons in the molecule are represented by a wave function, \(\psi\). The wave function itself does not have any intuitive physical meaning, but \(|\psi|^2\) describes the probability of finding the electrons in a region of space. \(\psi\) is a function of the position and spin of all the electrons in the molecule. Since each electron interacts with not only the atomic nuclei but also every other electron in the molecule, the solution of the Schrödinger equation is a many body problem. Even simple molecules typically have dozens of electrons, and molecules with large atoms or a large number of atoms can easily have hundreds or thousands of electrons. For example, CuI\(_2^-\), a three atom ion, has 136 electrons. The number of interactions between the electrons makes calculations unmanageable without simplifying assumptions.
The most basic level of theory is the Hartree-Fock approximation. In a Hartree-Fock calculation, the multi-electron wave function described by the Schrödinger equation is replaced by a product of \( N \) one electron wave functions. These single particle Schrödinger equations are far simpler to solve computationally and the complexity of the simulation is greatly reduced. However, the correlation between the electrons in the molecule are lost in the Hartree-Fock approximation. The loss of this information means that the simulation can never calculate the true wave function of the molecule [99]. As a result, Hartree-Fock often produces molecule geometries with significantly higher energies than the true geometry.

Another approach to simplify the solution of Schrödinger’s equation is density functional theory (DFT) modeling. DFT does not calculate the wave function, \( \psi \), but instead calculates the electron density, \( \rho \), which is related to \( |\psi|^2 \). The electron density is a function of only three spatial coordinates. The result of this approach is that many DFT methods use comparable computational resources to a Hartree-Fock simulation but provide accuracy comparable to that of more advanced wave function based methods. For that reason, DFT methods were used to calculate the UV-vis spectrum of \( \text{CuI}_2^- \). While wave function based methods were also attempted, the large number of electrons required more disk space than was available for the calculation.

Two DFT levels of theory were used to calculate the UV-vis spectrum, B3LYP and M06-2X. B3LYP is a hybrid method which combines DFT and Hartree-Fock methods to improve the accuracy of both methods while preserving the computational speed of the methods [100]. B3LYP is one of the most commonly used levels of theory in quantum chemistry [99]. M06-2X is also a hybrid method which includes additional interactions between the spins of different electrons known as the non-local exchange [101]. The calculations in this work were performed using the commercial quantum chemistry package Gaussian09.

The level of theory in a quantum chemical simulation describes the model of how a molecule’s electrons interact with one another and the atomic nuclei. To perform a simulation of a molecule, some model of the molecule must be developed for the level of theory to act
on. This model is given to the solver as a collection of atoms with an approximate geometry. The atoms and their electrons are described by the basis set. The basis set is a collection of functions, known as the basis functions which are combined linearly to develop a model of the molecular orbitals [99].

One type of common basis function is the Gaussian type orbital (GTO). The GTO is commonly used in Hartree-Fock calculations due to the computational methods available for solving integrals of Gaussian orbitals. A basis set with one GTO per electron orbital per atom is known as the minimum basis set, because it contains the minimum amount of basis functions needed to describe the atoms in a molecule [99].

The accuracy of a ab initio model may be improved by using a basis set which more realistically represents the molecular orbitals. An improvement on the GTO functions used in minimal basis sets is the Slater type orbital (STO) which more realistically models the cusps of orbitals. Other basis sets use Riemann zeta functions to model electron orbitals, which offer higher precision at a higher computational cost [99].

Both copper and iodine are very large atoms, and require a large basis set with many basis functions to describe their possible electron orbitals. The basis set used in this study is the aug-ccpV5Z-PP basis set. The ‘aug’ signifies that the basis set has been augmented by the addition of diffuse functions to capture the very large outer electron orbitals of heavy atoms. ‘ccp’ stands for ‘correlation-consistent-polarized’, meaning that the basis set produces orbitals that converge towards the ideal solution that includes electron correlation. ‘V5Z’ signifies that each valence electron orbital is modeled with five zeta functions. Finally, ‘PP’ stands for ‘pseudo-potential’. Iodine and copper both contain large numbers of core electrons. Modeling each electron individually in such a large atom is computationally expensive, and at the energies associated with UV-vis absorption bands only the valence electrons participate in transitions. The core electrons in this basis set have been lumped together into a relativistic pseudo-potential that acts on the valence electrons. This approach greatly reduces the computational cost of the basis set while providing good accuracy [102].
Once the appropriate level of theory and basis set have been chosen, the absorption spectrum may be simulated. First, a molecular geometry must be calculated for the ground state. The geometry, including bond lengths, and angles is calculated by an energy minimization. Once the geometry has been optimized, a frequency calculation may be completed to determine the vibrational frequencies, the IR spectrum, and Raman spectrum of the molecule. A B3LYP frequency calculation was used to predict the IR. For the CuI$_2^-$ ion, two IR peaks at 67 and 264 cm$^{-1}$ were predicted. A Raman peak at 128 cm$^{-1}$ was also calculated. While the IR peaks could be used for optical diagnostics, the peaks are located in the very low IR frequencies. In this far IR spectral region, optical materials such as CsI are typically used for windows and other optics. These optical materials are not compatible with the aqueous catholyte. Increasing the range of the FTIR to cover the very far IR would also require an expensive upgrade. The Raman peak could also be investigated as an optical diagnostic if an appropriate Raman spectrometer system were constructed or purchased. However, the UV-vis region of the spectrum allows the use of materials such as UV-fused silica, which is mechanically robust and inexpensive. For this reason, the UV-vis spectrum of CuI$_2^-$ was calculated.

Since the transitions that absorb in the UV-vis are electronic, we must calculate the excited states of the molecule. To simulate the transitions of the electrons between states of the molecule, we must solve the time dependent Schrödinger equation. Time dependence is captured by the TD-B3LYP and TD-M06-2X levels of theory. A molecular geometry is required at each of the excited states. This geometry may either be assumed to be the same as the ground state geometry, or the geometry may be recalculated via an energy minimization at each excited state. Calculations that use the ground state geometry for all excited states are known as vertical excitation calculations. If the geometry is recalculated at each excited state, the calculation is referred to as a adiabatic excitation. For this study, vertical excitations were carried out for the lowest 20 excited states. The excited state energy was calculated for both the singlet and triplet spin states at each state. Vertical excitations
were used to save computational time, since the optimization step at each excited state is computationally expensive.

### 4.7 Comparison of ab initio results and experimental measurements

To evaluate the accuracy of the computational results, experiments were carried out to determine the molar absorption coefficient, $\epsilon$, of CuI$^-$.

Since the CuI$^-$ ion is not stable in solution without the presence of $I^-$, the absorption spectrum of a mixture containing a known concentration of CuI$^-$ was measured and the other components were subtracted to isolate the absorption due to CuI$^-$.

A solution of CuI$^-$ and KI was prepared. The absorbance of this sample was measured using pure DI water as a baseline. The absorption spectrum of NaI and KI were also collected in a similar manner. Measurements of the absorption spectra of I$_2$ and I$_3^-$ were taken from published studies, which carefully controlled the concentration of I$_2$ and I$_3^-$ by equilibrating a solution with an adjusted pH and temperature for several days to obtain a quantitative absorption spectrum [103, 104]. For the mixture containing CuI$_2^-$, if the molar absorption coefficients are assumed to add linearly (Equation 1.24), the known absorption spectrum of KI may be subtracted from the mixture absorption spectrum. The concentrations of I$_2$ and I$_3^-$ are not known, but we may measure them from peaks which do not overlap with the other species present in the mixture. I$_3^-$ concentration may be measured from the 353 nm peak, and I$_2$ may be measured from the 460 nm peak (Figure 4.7).

Figure 4.8 shows the experimentally isolated absorption spectrum of CuI$_2^-$ and the results of the DFT models. Table 4.1 list the electronic transitions that make up the UV-vis spectrum of CuI$_2^-$.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Oscillator strength</th>
<th>Spin</th>
<th>Number of Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>259.32</td>
<td>0.0078</td>
<td>Singlet</td>
<td>1</td>
</tr>
<tr>
<td>265.13</td>
<td>0.0106</td>
<td>Singlet</td>
<td>1</td>
</tr>
<tr>
<td>267.02</td>
<td>0.0512</td>
<td>Singlet</td>
<td>3</td>
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<tr>
<td>285.71</td>
<td>0.0038</td>
<td>Singlet</td>
<td>4</td>
</tr>
<tr>
<td>297.21</td>
<td>0.0464</td>
<td>Singlet</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4.1: The electronic transitions calculated by the TD-B3LYP/aug-ccpV5Z-PP method.
Figure 4.7: The absorption cross-section of species that may be present in the sodium-copper-iodide cell. Absorption data for $I_3^-$ and $I_2$ were found in literature [104]. NaI was measured at temperature due to the temperature dependence of the charge transfer band. CuI$_2^-$ was measured in dilute KI solution and the spectrum corrected for the presence of KI.

In Figure 4.8, the quantum chemical results give the absorption spectrum as discrete spectral lines associated with individual electronic transitions. The intensity of each line is given as a dimensionless oscillator strength, which is related to the probability that the transition will absorb an incident photon of the correct energy. The oscillator strength, $f$, is related to the molar absorption coefficient by

$$f = 1.875 \times 10^{-9} \int_{\nu_0}^{\nu_f} \epsilon(\nu) d\nu$$

(4.28)

where epsilon is the natural log based molar absorption coefficient and $\nu$ is the frequency in wavenumbers. $1.875 \times 10^{-9}$ (cm$ \cdot$ mol) is a constant derived from the Einstein coefficient of a generic electronic transition. The integral term accounts for the energy of the specific transition. $\nu_0$ and $\nu_f$ are the low frequency and high frequency limits of the spectral band associated with the transition of interest [105, 106].
While an absorption band may be constructed from the oscillator strengths by assuming a line shape and broadening parameters, spectra from quantum chemical models are usually reported as line locations. The calculation of oscillator strengths by ab initio models is very sensitive to errors in the electron correlation model and tends to be less precise than the energy calculations that determine the location of spectral lines [107]. Therefore in Figure 4.8, the ab initio results are presented as discrete lines rather than broad peaks.

The spectral line locations are generally correct for B3LYP/aug-ccpV5Z-PP, although the spacing between the lines is somewhat larger than the experimental results. M06-2X/aug-ccpV5Z-PP over predicted the excited state energies, leading to spectral line locations that are shorter wavelengths than the experimental data. The error in the M06-2X calculations is most likely due to the copper atom of the ion. M06-2X is parametrized for non-metals,
leading to errors in the energy calculations of the ion’s excited states [101].

4.8 Optically accessible battery

In order to probe the chemical reactions occurring inside the sodium-copper-iodide cell, it was necessary to construct an electrochemical cell with optical access. The design for the optical battery was required to meet the following criteria:

- Provide optical access to the cathode and catholyte solution in the UV-visible range of the spectrum to allow spectroscopic measurements of light transmitted through the catholyte solution.

- Seal a cathode chamber containing aqueous sodium iodide from an anode chamber containing molten sodium metal. The two chambers must also be separated by a thin (∼1 mm) Nasicon ion exchange membrane. This thin strip allows ion exchange between the anode and the cathode. The Nasicon membrane must be as thin as possible to reduce the ohmic losses in the cell.

- Allow fluid and electrical connections from outside the battery to the cathode chamber. Fluid connections were required to pump catholyte into and out of the cathode chamber. The anode chamber required electrical connections to the outside.

- Materials with the ability to operate at 110 °C and withstand a sodium wetting heat treatment at 150 °C.

The first concept for the optical battery is shown in Figure 4.9. The cell design was based on the Specac GS20730 heated liquid transmission cell. This cell consisted of a two-piece metal housing which compressed a pair of optical windows separated by a spacer. Different spacers were used to provide different pathlengths. Fluids were introduced through a pair of holes drilled in the front window of the cell. The front half of the metal housing is designed with fill ports which line up with the drilled window. The window and metal housing were
separated by a Teflon® gasket to prevent leaks from the fill port and also to cushion the metal-to-optic interface.

Using the Specac cell as a starting point, the cell in Figure 4.9 was designed. The cell design replaced the original Specac spacer with an “ion exchange structure”. The ion exchange structure includes the ion exchange membrane as well as the chambers for the anode and cathode of the battery. The ion exchange structure was machined from a 1 mm thick 4 in diameter disk of Nasicon, which was donated by Coorstek.

![Figure 4.9: a and b: The original optical battery concept. This design was built off of the Specac heated cell system. The design required machining windows to accommodate the fluid and electrical connections of the battery, which proved to be a weak point in the design. The holes for the electrical connections combined with the windows bearing the compression load from the cell housing lead to the windows cracking. c: Detail of the optical access. The 1 mm gap between the cathode and the Nasicon ion exchange membrane allows a light beam to be focused into the region where a concentration gradient of CuI$_2^-$ is anticipated.

Sealing of the cathode and anode chambers was accomplished by means of laser cut Viton® gaskets. The gaskets included a 2×4 mm rectangular hole to allow optical access
into the cathode chamber.

The ion exchange structure and gaskets were sandwiched between a pair of custom machined CaF\textsubscript{2} windows. The front window was machined with four holes to allow a $\frac{1}{16}$ in diameter tube to pass through the window into the ion exchange structure. The holes in the windows were sealed with IDE\textsuperscript{X} Health Science Nanoport fittings (IDEX PN: N-333). The Nanoport fittings consist of a ferule and nut system that slide over the tubing leading into the cell and screw into a threaded fitting which is glued onto the window with a suitable adhesive. Finally a custom metal housing was machined to compress the assembled cell without interfering with the Nanoport fittings.

After experimenting with the initial cell design, a number of shortcomings were noticed. First, the cell required extensive machining of the windows. Windows were obtained as round blanks from International Crystal Laboratories and then cut with a CNC mill and diamond tooling into the appropriate shape. The front window was then drilled to allow the fluid and electrical connections through the window. Since the windows are a brittle material, the milling operation involves slowly grinding material away rather than cutting chips of material. Grinding requires very slow feedrates and therefore long machining times. The holes drilled in the windows also weakened the windows, which frequently cracked when they were compressed by the metal housing and heated.

The Nanoport fittings also proved to be a weak point in the cell design. The Nanoport fitting must be attached to the window with an adhesive. The cell operates at 110 °C and must be heat treated at 150 °C to wet the sodium to the Nasicon ion exchange membrane. No suitable adhesive was found that could withstand multiple thermal cycles and exposure to the catholyte. The Nanoport fittings frequently delaminated from the windows and leaked.

Finally, the Viton\textsuperscript{®} were incompatible with the battery chemistry. The Viton\textsuperscript{®} polymer contains fluorine, which is attacked by the molten sodium. Over time the Viton\textsuperscript{®} broke down and contaminated the catholyte solution with fine black particles which made accurate spectroscopic measurements impossible.
The design of the cell was refined to prevent window cracking and cell leaks (Figure 4.10). First, since optical access was only required in a small part of the cathode chamber, the large custom machined windows were replaced by 5 mm diameter, 1 mm thick UV fused silica windows from Edmund Optics (Edmund PN: 45-463). UV fused silica windows have a higher fracture toughness and are less susceptible to thermal shock than calcium fluoride. The metal housing was redesigned to include pockets for the windows to sit flush with the surface of the housing. In the refined cell design, most of the compressive load from the housing is carried by the aluminum of the housing itself, rather than the optical material. This design change reduced the likelihood of window cracking.

![Diagram of revised cell design](image)

**Figure 4.10:** The revised cell design. Smaller windows were used to avoid machining the windows or using the optical material to bear the compressive load from the aluminum housing. Ports for the fluid and electrical connections were machined directly into the aluminum housing. The housing was also designed to allow a smaller Nasicon ion-exchange structure to be used; reducing the amount of Nasicon needed in each cell.

The new design also has a pocket which accommodates the ion exchange structure. This pocket allows a smaller ion exchange structure to be aligned inside the cell, which reduces the amount of Nasicon needed to operate the cell.

Finally, the Viton® gaskets were replaced with EPDM rubber, which is more resistant to molten sodium. Teflon gaskets were placed between the aluminum housing and the EPDM
gaskets to prevent the EPDM from sticking to the housing.

Figure 4.11 shows a diagram of the experimental apparatus used to test the optically accessible cell. The cell was secured in a standard spectroscopy slide holder to prevent movement of the cell during the test. The cell was illuminated with a deuterium halogen lamp, and transmitted light was collected by a fiber optic and measured by an Ocean Optics Maya2000+ UV-vis spectrometer with a spectral range of 165-615 nm and a resolution of 0.47 nm. The spectral range of measurements was limited to wavelengths longer than 180 nm due to attenuation by the fiber used to collect light.

Electrochemical measurements were performed with an EZStat Pro potentiostat configured for a two-electrode experiment. The anode was used as the counter/reference electrode and the cathode was used as the working/sense electrode. The leads of the potentiostat were connected to copper wires passed through the fluid connections of the cell into the anode and cathode chambers.

4.9 Experimental results

Results from the testing of the optical cell were mixed. The concentration of NaI was able to be determined from spectroscopic results. Figure 4.12 shows a comparison of the measured concentration of NaI and the concentration calculated from the total charge passed through the cell using Equation 4.11. Agreement between the two methods is very good until about 160 min into the test, at which point the catholyte in the cell crystallized. At this point, no further electrochemical reactions were possible and the cell began to act as a resistor.

The concentration of NaI in the cell was measured optically by monitoring the change in absorbance at 225 nm where NaI shows strong absorption. Recalling the Beer-Lambert law, Equation 1.22, since the pathlength of the cell and the molar absorption coefficient, $\epsilon(\lambda)$, are both known, the concentration may be determined from an absorbance measurement.

$$-\ln \left( \frac{I}{I_0} \right) = \alpha(\lambda) = \epsilon(\lambda)cL$$

(4.29)
where $\alpha(\lambda)$ is the absorbance as a function of wavelength. In Figure 4.12, the spectrum of the cell filled with catholyte at time 0 was used for $I_0$, so $\alpha$ at time $t$ is used to calculate a change in the concentration of NaI from time 0 to time $t$. Due to the large molar absorption coefficient of NaI, even small changes in concentration produce a large change in the observed absorbance, allowing measurements to be made with a high signal to noise ratio.

In Figure 4.12, the change in concentration of NaI was determined electrochemically from the cell current. For this test, the cell was connected to a Keithley 6482 picoammeter and voltage source. The cell was charged by applying a constant 3.1 V potential to the cathode of the cell. The high resolution of the picoammeter ($\sim 1$ fA) allowed very precise measurements to be made of the cell current. The cell current and a UV-vis spectrum of the transmitted light were recorded at 1 s intervals. Since current is the flow of charge over time, we can
Figure 4.12: The concentration of NaI measured spectroscopically compared to the concentration calculated from the total charge passed through the cell with $N = -1$. The value of $N = -1$ agrees with the predicted change in the concentration of NaI if the complexation of CuI to CuI$_2^-$ is slow compared to the formation of CuI on the cathode surface.

use Faraday’s law (Equation 4.11) to determine the change in concentration of NaI if the reaction stoichiometry is known. The change in concentration may be determined by

$$\Delta c_{\text{NaI}}(t) = \frac{Q(t)}{NF} = \frac{1}{NF} \int_0^t i_{\text{cell}}(t) dt$$

(4.30)

where $c_{0,\text{NaI}}$ is the initial NaI concentration, $F$ is Faraday’s constant, $Q(t)$ is the total charge that has passed through the cell at time $t$, and $i_{\text{cell}}(t)$ is the current flowing through the cell as a function of time. $N$ is the stoichiometric ratio of the number of electrons transferred by the cell reaction to the number of I$^-$ ions consumed by the reaction. Recall that for the cathode half cell reaction during charging

$$\text{Cu}_\text{(s)} + 2\text{I}^-_{\text{(aq)}} \longrightarrow \text{CuI}_2^-_{\text{(aq)}} + \text{e}^-$$

(4.31)

Since two I$^-$ ions are consumed for every electron liberated by the reaction, $n$, is expected to be $-1/2$. However, good agreement between the electrochemical and spectroscopic measurement are seen in Figure 4.12 for $N = -1$. 

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In order to understand this result, we consider the cathode half cell reaction again. In Equation 4.31, we showed the half cell reaction as a single step. In reality, the half cell reaction occurs in two steps, the formation of CuI on the surface of the cathode followed by complexation with a second I$^-$ ion to form Cu$I_2^-$.

\[
\text{Cu}(s) + I^-(aq) \rightarrow \text{CuI}(s) + e^-
\]  

(4.32)

\[
\text{CuI}(s) + I^-(aq) \rightarrow \text{CuI}_2^-(aq)
\]  

(4.33)

The stoichiometric ratio $N = -\frac{1}{2}$ assumes that the complexation step of the cathode half cell reaction is fast. For $n$ to be equal to $-\frac{1}{2}$, CuI must be complexed as soon as it is formed on the cathode surface. Note that if the reaction in Equation 4.33 is slow, fewer I$^-$ ions will be consumed in the reaction. If the complexation of CuI is much slower than the formation of CuI, then the stoichiometric ratio $n$ will be effectively -1. The results shown in Figure 4.12 therefore suggest that the complexation of CuI to Cu$I_2^-$ is slow compared to the formation of CuI on the cathode surface.

These results demonstrate the value of simultaneous electrochemical and in-operando optical diagnostics. Because the complexation step of the cathode half cell reaction (Equation 4.31) does not involve the transfer of electrons, electrochemical methods alone are not able to determine the concentration of NaI in the catholyte. By coupling optical diagnostics to the electrochemical methods, we are able to determine that the stoichiometric ratio is approximately -1, rather than $-\frac{1}{2}$.

While the results shown in Figure 4.12 are promising and demonstrate the usefulness of in-operando spectral measurements, further tests showed that designing an optically accessible cell for transmission measurements leads to significant difficulties. Several competing design requirements made the design of a heated optical battery challenging. First, a working cell requires the anode and cathode to be electrically isolated from one another by an ion exchange membrane. Without electrical insulation, the cell will short circuit and no current will be stored or released from the cell. In the case of the Na-Cu-I$^-$ chemistry, since the
anode is elemental sodium and the catholyte is aqueous, any failure in the sealing of the cell will result in a vigorous reaction between the sodium and the water. This reaction will fill the cathode chamber with hydrogen gas, disrupting the optical baseline of spectroscopic measurements. Figure 4.13 shows an example of the baseline shifts seen during battery tests.

![Graph showing baseline shift](image)

Figure 4.13: An example of the typical baseline shifts seen during the course of a test. The shift in the optical baseline is large compared to any changes in the spectrum due to changes in the electrolyte composition.

To prevent leaks and ensure a stable optical baseline, reliable sealing of the cathode and anode chambers is required. Seals between two flat faces are usually formed through the use of gaskets. Gaskets are thin sheets of material that deform under the clamping pressure of the joint to fill in gaps between the faces being sealed. At high temperatures, many materials experience creep. Creep is a gradual plastic deformation of the material over time at elevated temperatures [108]. When gaskets are heated, creep can cause the gasket to compress further, resulting in a loss of clamping force on the joint. Belleville spring washers may be used to compensate for some of the lost clamping force. Sealing a joint that undergoes thermal cycling requires providing sufficient clamping force to seal the joint even after the gasket has experienced creep without over stressing the gasket and the faces being
sealed. In this work, the gasket material was limited to EPDM rubber due to the need for materials compatibility with molten sodium. The EPDM used in the optical battery has a maximum service temperature of 150 °C. Since the cell operates at ~100 °C, the gaskets were affected by creep.

In the optical battery, ensuring a seal between the Nasicon and EPDM gaskets without stressing the Nasicon to the point of failure was not feasible with a cell optimized for transmission measurements. The mechanical stability of the Nasicon proved to be a significant problem. Tests were carried out to determine the minimum clamping force needed to establish a water-tight seal of the cathode chamber. A plastic model of the Nasicon ion exchange structure was prepared and clamped in the cell housing with EPDM gaskets identical to those used in tests of the real cell. The plastic ion exchange structure was laser cut from a sheet of material of similar thickness to the real ion exchange structure. A torque screwdriver was used to tighten the machine screws used to hold the halves of the cell together. The minimum torque on the screws which produced a water-tight seal with the softest gaskets (durometer 40A) was 20 in·oz. Even with this minimum clamping force, hairline fractures formed in the ion exchange structure that allowed the molten sodium to wick out of the anode chamber. Figure 4.14 shows the cracking which caused the cell to fail repeatedly and the optical baseline to shift.

As can be seen in Figure 4.14, the fracture formed at the circular radius of the anode chamber left by the milling operation. This location is where the largest stress concentration is predicted to occur [109]. The transmission cell requires the Nasicon to be machined into an ion exchange membrane with small features. This membrane must then also be sealed, requiring the Nasicon to be subjected to a clamping force. The fine features combined with the brittle properties of Nasicon result in a cell that cannot be adequately sealed.

The transmission geometry also results in a cell which has a large gap between the cathode and the Nasicon. The gap in the optical battery was approximately 1 mm. In most real batteries the cathode is in intimate contact with the ion exchange membrane [110].
Figure 4.14: The cell after failure. The Nasicon ion exchange structure developed a hairline crack which allowed molten sodium to wick out of the anode chamber to the exterior of the cell (right hand side).

This gap results in high cell resistance, since the electrochemical species must diffuse across the gap from the membrane to the electrode to participate in the reactions on the surface of the electrode. Figure 4.15 shows voltammograms from cyclic voltammetry experiments. The current passed through the cell when it is filled with electrolyte is a similar order of magnitude when the cell is filled or empty, indicating that the cell resistance is very high.

While the optical battery experienced serious problems with reliability and stability, a diagnostic for measuring the concentration of CuI$_2^-$, I$^-$, I$_2$, and I$_3^-$ with UV-vis spectroscopy has been developed. The absorption spectra of each component may be loaded into a linear least squares solver (Appendix A) to determine the concentration of each component in an unknown spectrum. The spectrum of the interesting CuI$_2^-$ ion has also been measured and compared to the results of DFT simulated spectra.
Very little current passes through the cell even when the cell is heated and filled with catholyte, indicating that the cell has a very high resistance.

4.10 Proposed cell design

The tests presented here show that an optical Na-Cu-I$^-\text{cell}$ will be prone to breaking, and producing reliable data will be difficult with a transmission design. A revised cell design, using $\text{attenuated total reflection (ATR)}$ would allow optical access to the cathode of the cell with the intricate machining of the transmission cell. ATR utilizes a light beam which is reflected inside of a crystal to perform absorption measurements. The crystal is shaped so that the light beam strikes a face of the crystal at an angle above the critical angle which is the angle at which all the light will be reflected internally. Along this face of the crystal, an evanescent wave extends a short distance ($\sim0.1$-$5 \, \mu\text{m}$), depending on the crystal used, index of refraction of the sample, and the wavelength of the light beam) beyond the crystal face. When the face with the evanescent wave is in intimate contact with a sample, the evanescent wave penetrates the sample and an absorption spectrum may be measured [13].

Although ATR is most commonly used with IR spectroscopy, UV-vis spectra may also be collected [111]. A concept for a cell making use of an ATR crystal is shown in Figure 4.16.
The ATR crystal is placed in intimate contact with a fine copper mesh so that the evanescent wave interrogates the catholyte at the cathode surface. This arrangement allows the cathode half cell reaction to be studied in detail. The advantage of the ATR cell design is that no machining of the Nasicon wafer is required. The stress concentrations which lead to cracking and cell failure in the transmission cell would be greatly diminished. The anode may be applied to one side of the Nasicon and a fine copper mesh cathode to the other. The contact between the Nasicon and the electrodes will allow for lower cell resistances and better performance.

Furthermore, the ATR cell design is broadly adaptable to other cell chemistries. The cathode, anode, ion exchange membrane, and electrolyte materials may be changed to allow various cell chemistries to be investigated.

The ATR technique may also be used with IR spectroscopy, which provides detailed information on the molecular bonds present in the cell electrolyte. For cell chemistries based
on organic solvents or ionic liquid electrolytes, IR spectroscopy may be used to monitor the thermal and electrochemical stability of the electrolyte. As has been shown in this work, specific bonds of ionic liquids may be monitored for thermal degradation. The rate at which the electrolyte is degraded may also be measured optically. Since thermal breakdown does not involve electron transfer, optical diagnostics will provide additional insight into the cell stability that cannot be obtained by electrochemical methods alone.
CHAPTER 5
CONCLUSIONS

Quantitative optical techniques allow measurements of species concentration, temperature, and other physical variables. Optical techniques are non-invasive, which allows measurements to be made without probes or sampling devices. Because they do not rely on sample devices, optical spectroscopy techniques are ideal for in-situ and in-operando measurements.

These techniques have been applied to develop diagnostics for liquid electrolytes. The first quantitative IR and UV-vis spectral data of a heated RTIL has been measured for [EMIM][EtSO₄]. These quantitative spectral data have been applied to investigate the thermal stability of [EMIM][EtSO₄]. Spectroscopy experiments carried out at temperature suggest that the ionic liquid is thermally stable for at least 1 hour at temperatures below 75 °C. The onset of thermal degradation is between 75 and 100 °C, and the apparent rate of degradation may be estimated to be 0.02 mol·L⁻¹·min⁻¹ from isothermal spectroscopic experiments.

This work is also the first investigation of RTIL thermal stability using optical methods. The use of IR spectroscopy allows specific bonds to be identified and monitored in-situ. The bonds associated with the sulfate group of the anion display the most significant degradation. These results are in good agreement with previous investigations into the thermal stability of the [EMIM][EtSO₄] ion pair, and the IR spectrum shows that this degradation is specifically associated with the SO bonds of the anion.

Quantitative spectral data of [EMIM][TFSI] and the common impurity MIM have been applied to provide sensing for process control in the industrial synthesis of [EMIM][TFSI]. A novel LED-based optical sensor was designed to measure the concentration of MIM in a [EMIM][TFSI] product stream. The measurement allows a continuous synthesis process to be
monitored in real-time to provide feedback control. Monitoring the synthesis process allows expensive purification steps in the industrial production of RTILs to be skipped, lowering the cost of the product.

The sensor was constructed using low cost components such as LEDs and photodiode detectors. These relatively inexpensive components allow the sensor to be constructed at a cost far less than even a simple laboratory spectrometer and light source. This sensor allows a continuous flow production process to be monitored automatically, which represents an important step towards providing affordable RTILs for a variety of applications. This sensor has been shown to detect MIM in [EMIM][TFSI] with a detection limit of 4 mol%.

Quantitative spectral data were collected for the I\(^-\) and CuI\(_2\)\(^-\) ions in aqueous solution. The UV-vis spectrum of CuI\(_2\)\(^-\) was also estimated from quantum chemical calculations. These spectral data were applied to a custom optically accessible battery cell to allow in-operando measurements of species concentrations in a Na-Cu-I\(^-\) battery chemistry based on the use of Nasicon ceramics as an ion exchange membrane. The cell was designed, fabricated, and tested using both electrochemical and spectroscopic techniques. Processes were developed for machining Nasicon. In-operando measurements of I\(^-\) concentrations were collected. The results of this measurement showed that the complexation of CuI to CuI\(_2\)\(^-\) is slow compared to the formation of CuI on the electrode surface. This determination is made possible by the combination of in-operando optical diagnostics and electrochemical techniques. Since the complexation of CuI to CuI\(_2\)\(^-\) does not involve the transfer of electrons between the anode and cathode of the cell, traditional electrochemical measurement techniques are unable to detect changes in the concentration of NaI in the electrolyte due to complexation. However, the optical diagnostics were able to determine that the stoichiometric ratio of electrons transferred through the cell to the I\(^-\) consumed in the electrochemical reaction was nearly 1:1 rather than the value of 1:2 expected if the kinetics of complexation are fast. Since the complexation process cannot be measured with electrochemical methods alone, this work is the first experimental investigation of relative kinetics of the complexation process and the
formation of CuI at the cathode surface.

The transmission cell repeatedly leaked, leading to very high cell resistance and shifts in the optical baseline. Failure analysis of the cell showed that the material properties of Nasicon limited the stability of the cell. Stress concentrations from the clamping force required to seal the cell lead to cracks in the Nasicon. These cracks compromised the sealing of the anode and cathode which resulted in leaks and unstable electrochemical and spectroscopic measurements.

The lessons learned from the failure analysis of the transmission cell have been incorporated into a design for a new cell that uses ATR spectroscopy to interrogate the cathode of the cell. ATR measurements allow for the well established button cell geometry to be used, resulting in better cell performance and more signal from optical methods. The design also eliminates the need for the fragile geometry of the transmission cell.

Overall, this work has demonstrated that optical diagnostics provide unique insight into the properties of electrolytes and electrochemical reactions taking place in electrolytes. IR spectroscopy’s ability to probe the molecular structure of samples provides detailed information on the bonds involved in the thermal breakdown process of [EMIM][EtSO₄]. Optical spectral data have been used to develop a low-cost sensing solution to the problem of quality control in the industrial synthesis of [EMIM][TFSI]. The non-invasive nature of optical diagnostics has allowed in-operando measurements of the concentration of NaI in the catholyte of a Na-Cu-I⁻ cell, providing insight into the cathode half cell reaction.
REFERENCES CITED


APPENDIX A - SPECTRAL FITTING CODE

function coeff=spectral_fit(varargin)
% Function to calculated mixture concentrations from component spectra
% Syntax: wavelengths to be fitted, spectrum to be fitted, component
% wavelength 1, component spectrum 1, ... component wavelength n,
% component spectrum n

% Returns column vector x from A*x=b, where b is the spectrum to be fitted, and A is the component matrix

% Assumes LINEAR absorption

% Define spectrum to be fitted
wavelengths=varargin{1};
spectrum=varargin{2};

components=zeros(length(wavelengths),(length(varargin)-2)/2);
k=3;
j=1;

% Define component matrix
% Components are interpolated to match wavelength values of the spectrum to be fitted
for i=3:length(varargin)/2+1
    components(:,j)=interp1(varargin{1,k},varargin{1,k+1},wavelengths,'linear',0);
    j=j+1;
    k=k+2;
end

if any(any(components))
    coeff=spectrum\components;
else
    error('spectral_fit: Component matrix must be non-zero. Check wavelength ranges')
end
end
APPENDIX B - OPTICAL CELL DRAWINGS

This appendix contains technical drawings of the optically accessible battery. The cell is designed to be compatible with the Specac heating jacket (Specac model GS20730). All dimensions in the drawings are given in inches.

The cell housing was fabricated from Aluminum alloy 2011, which is designed for easy machining. The ports to accommodate the fluid and electrical connections are tapped with 10-32 threads. These threads are compatible with 10-32 fittings from IDEX Health science, such as PN XLT-111X. These fittings consist of a hollow threaded nut and a ferrule which can be threaded into the tapped hole. Tubing is run through the hollow nut, and the ferrule forms a seal when the nut is tightened. A 1/16 in PFA tube was used for fluid connections and the electrical wires were run inside the tube. The wire, 32 AWG uncoated solid copper, was used for the cathode as well as the anode charge collector.

The ion exchange structure of the battery is machined from 1 mm thick Nasicon blanks obtained from Coorstek. Due to the brittle nature of Nasicon, traditional cutting endmills are not suitable for Nasicon machining. Instead, solid core diamond drill bits are used to grind through the Nasicon. 2 mm diameter diamond drill bits were obtained from UKAM Industrial Superhard Tools (UKAM PN: 4ED20). Since machining the Nasicon is a grinding rather than a cutting operation, high tool speeds and low feedrates are required. The tool speed used for machining the Nasicon was 6000 RPM, he maximum possible on the Haas Mini Mill 2 CNC used for machining the Nasicon. The Z direction feedrate was 0.02 in/min and the X-Y feedrate was 0.04 in/min. With these settings, cutting the ion exchange structure takes about 10 hr. If higher tool speeds are available, the feedrates may be increased to allow for faster machining. The exact feedrates for a given tool speed that result in the best surface finish will required experimentation.
Windows for the cell were obtained from Edmund Optics. The cell is designed for 5 mm diameter, 1 mm thick windows. The UV fused silica windows used are Edmund Optics PN 45-463. The widows were affixed to the cell using Norland Optical Adhesive 61.

The full assembly fits snugly inside the Specac electric heating jacket, which allows temperature control of the cell.
CELL HOUSING: FRONT
TAP 10-32 X2

Φ0.21

Φ0.06 X2

TAP 4-40 X6

0.26

0.04

0.56

CELL HOUSING: BACK

Φ0.16

TAP 10-32 X2

Φ1.00

Φ1.62