SAND2018-2835J

Spectral Processing

The first step in spectral processing was to remove cosmic ray interference with a filter size and dynamic factor of 4 using the WiTec Project software. The filter size determines the total window over which each point is evaluated. The window size is 2*(filter size) + 1. The dynamic factor determines the sensitivity of cosmic ray removal.

In most cases, spectra were obtained as a long-time series, meaning that each accumulation was recorded separately. This was done to be able to track if peaks were changing during spectra acquisition. This also aids in the removal of the cosmic ray background. The downside to this is that this increases the read error of the spectra because the CCD counts must be read into the computer multiple times rather than just once. However, this error is small in contrast to the benefits of being able to see changes in peaks. The accumulations were averaged together into one spectrum.

The background of each spectrum was subtracted by using MATLAB® software to fit a piecewise cubic hermite interpolating polynomial (PCHIP) to minima on the spectrum. The minima were determined by looking at 5 points below and above a hand-picked point and taking the minimum value. Doing this helped to minimize any loss of data. The use of PCHIP rather than a normal spline prevented any unintended waves between interpolation points. An example of a raw data set, in the region of interest, and its background subtraction is shown in Figure S1.

All spectra were then put in terms of CCD counts per second and normalized to the maximum value that most closely corresponded to the 740.7 cm^{-1} LiTFSI peak. Therefore, all normalized peaks where LiTFSI was in the system are relative to this peak. LiTFSI should not change in intensity and thus is a good peak to compare to.

Once normalized, the spectra were scaled by multiplying by an average scale factor determined by the value needed to match the 280 and 740.7 cm^{-1} peaks in the sample to that of the electrolyte with its background removed. This only adjusted the spectra slightly since their peak at 740.7 cm^{-1} was already equal to 1. The absorptivity of the polysulfides was wavelength-dependent. Using an average scale-factor helped mitigate the changes in electrolyte peak intensity due to the absorptivity of polysulfides at different wavelengths above approximately 200 cm^{-1} and below 600 cm^{-1}. An example of this method is shown in **Error! Reference source not found.**. It can be seen from **Error! Reference source not found.** that above approximately 600 cm^{-1} there are still intense electrolyte peaks present. This lack of complete subtraction is due to the change in absorptivity outside the polysulfide Raman-active range. Since all polysulfide peaks, excluding the dithionite anion peak at 1066 cm^{-1}, were below 600 cm^{-1}, it was not necessary to fit an additional wavelength-dependent scaling factor to subtract electrolyte peaks above 600 cm^{-1}.

In cases where LiTFSI was not present, values were normalized by conventional means where normalized value = (raw value - minimum) / (maximum – minimum).

In situ T-Cell

The *in situ* T-cell setup is depicted in Figure S5. A normal discharge curve of the *in situ* cell at a rate of C/50 is shown in Figure S12.

Raman Analysis of System Components

Individual spectra of DOL, DME, LiTFSI, and $LiNO_3$ are depicted in Figure S3A-D and the full electrolyte spectrum is shown in Figure S3E. The spectra in Figure S3 are normalized, but do not have their backgrounds subtracted (other than subtraction of the dark spectrum) in order to show background fluorescence that can potentially obscure the signal from polysulfides during *in situ* measurements. As shown, none of the spectra have a large fluorescence background. All spectra in Figure S3 were obtained using the 10x objective and an optimized power of 8 mW with 30 seconds integration time and 10 accumulations. Raman spectra of S_8 and Li_2S are given in Figure S4.

Consistent within two wave numbers of the results of Suo et al.[22], pure LiTFSI has its most intense peak at approximately 748.9 cm^{-1} (747.3 cm^{-1} Suo et al.) while 1 M LiTFSI in the electrolyte is located at approximately 741.5 cm^{-1} (740.7 cm^{-1} Suo et al.).

The electrolyte exposed to air, both alone and with polysulfides present, experienced an increase in the fluorescence background, in the region of interest for polysulfides, as seen in Figure S8. In some cases, at longer exposure times, the increase was so intense, that smaller peaks were difficult to distinguish from the background, therefore it was important for all experimental components to remain under argon in order to obtain useful spectra. Additionally, some photo-bleaching was observed, especially when exposed to oxygen. If lower powers and longer integration time were utilized to decrease photo-bleaching, the spectrum became noisy, the fluorescence background increased, and peaks were difficult to identify. The fluorescence background could also be increased through the introduction of contaminants, thus sample preparation and cleaning, including sonication, were found to be important.

Next, the solvent and LiTFSI were analyzed separately to pinpoint the source of the fluorescence. 1:1 DME: DOL did not show any change from that of Figure S3 A and B when decreasing the power below 8 mW. LiTFSI however, appeared to be the source of photo-bleaching and the large fluorescence background. This was studied by taking a spectrum every 2 seconds, 30 times. Representative spectra across the 60 second experiment are shown in Figure S9A. This photobleaching behavior was not observed when the same experiment was performed under argon (Figure S9B). The background and peaks remain consistent when analyzed under argon with the exception of peaks near 142 and 274 cm^{-1} which decrease in intensity with increasing illumination time. The power of 8 mW, optimized for the liquid electrolyte, is too intense for solid LiTFSI. However, since the Raman laser can be used to study both solids and liquids, it is important to know how both solids and liquids behave under the optimized power. Figure S6 shows that the optimized 8 mW power did not damage the liquid samples.

Raman of Lithium Polysulfide Standards

The nominal Li_2S_8, Li_2S_6, and Li_2S_4 standards in argon, 17 hours from reaction initiation, and their variability between two replicates, are depicted in Figure 1 of the article. The background and electrolyte peaks were subtracted to more clearly identify the polysulfide peaks, especially in cases where polysulfide and electrolyte peaks overlapped.

Despite differences in reactant stoichiometry, the three standards equilibrate to have the same species present and have similar peak positions (though peak intensities still vary between the three standards). Several polysulfide assignments from the literature are within a few wave numbers of broad peaks, such as ~390 and 450 cm^{-1}.[24] These broad peaks are most likely a combination of multiple peaks for several polysulfide chain lengths.

The three standards can be distinguished from each other through differences in coloration (Figure S11) and relative peak intensities.

The peak intensities were obtained by fitting the peaks to a Lorentzian function which provides information on the peak intensity, full width half max (FWHM), and peak position.

The peaks at 390 and 450 cm^{-1} are more difficult to fit to a Lorentzian function due to some irregularities in peak shape including peaks that have a plateau or bumps at the top of the peak and bumps off-center from the peak maximum. This is most likely due to the presence of several peaks combining to form the observed broad peaks. Additional analysis using techniques such as multivariate analysis would be required to further analyze these peaks; but for this effort, these methods were deemed sufficient for the analysis.

Fitting to a Lorentzian function provides a consistent method of determining peak intensities, however the FWHMs from the fits have large confidence bounds. Only peak intensity and position were tracked.

In cases where fitting a peak was not relevant (e.g. a peak had too low of an intensity), the intensity of the spectrum rather than the intensity of the fit was recorded.

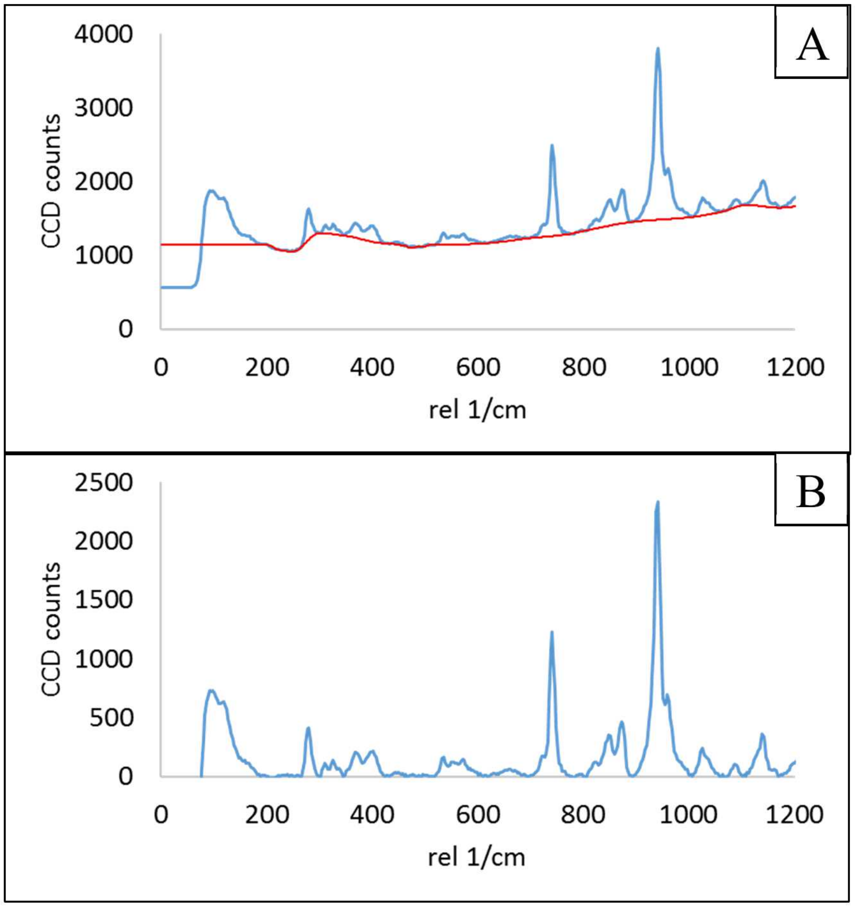

Figure S1: Example of background subtraction for a Li_2S_8 standard A.) before and B.) after background subtraction.

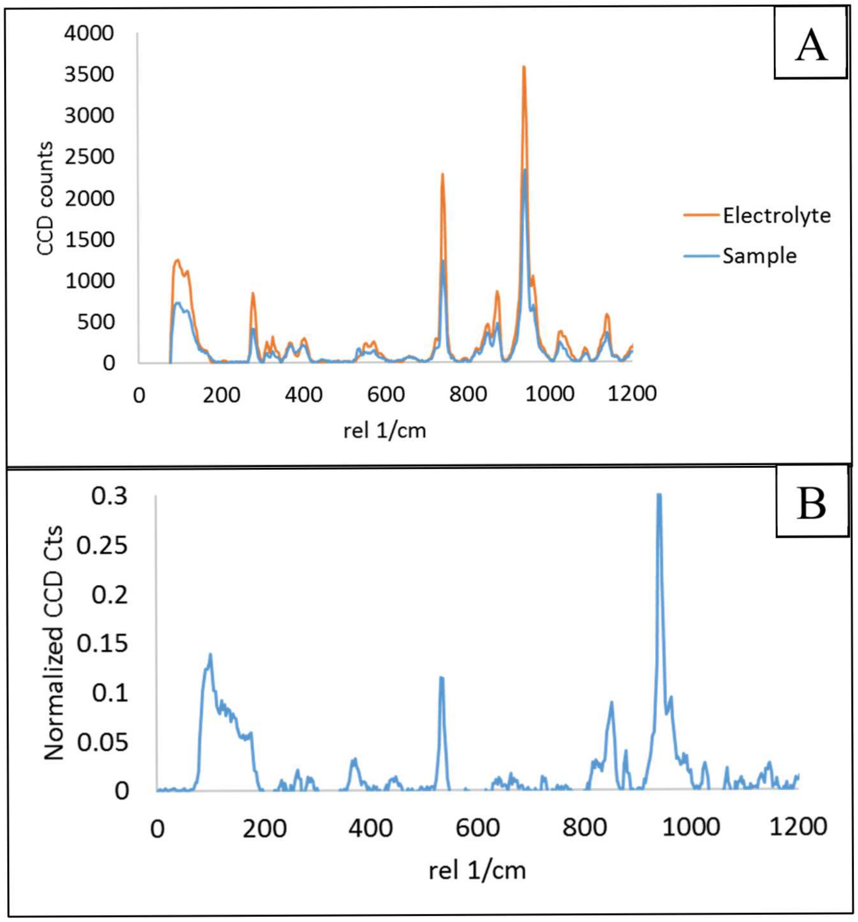

Figure S2: Example of normalization to the 740.7 cm^{-1} LiTFSI peak and subtraction of electrolyte peaks where A.) is a comparison of the electrolyte and a Li_2S_8 standard prior to normalization and electrolyte subtraction and B.) is after normalization and electrolyte peak subtraction.

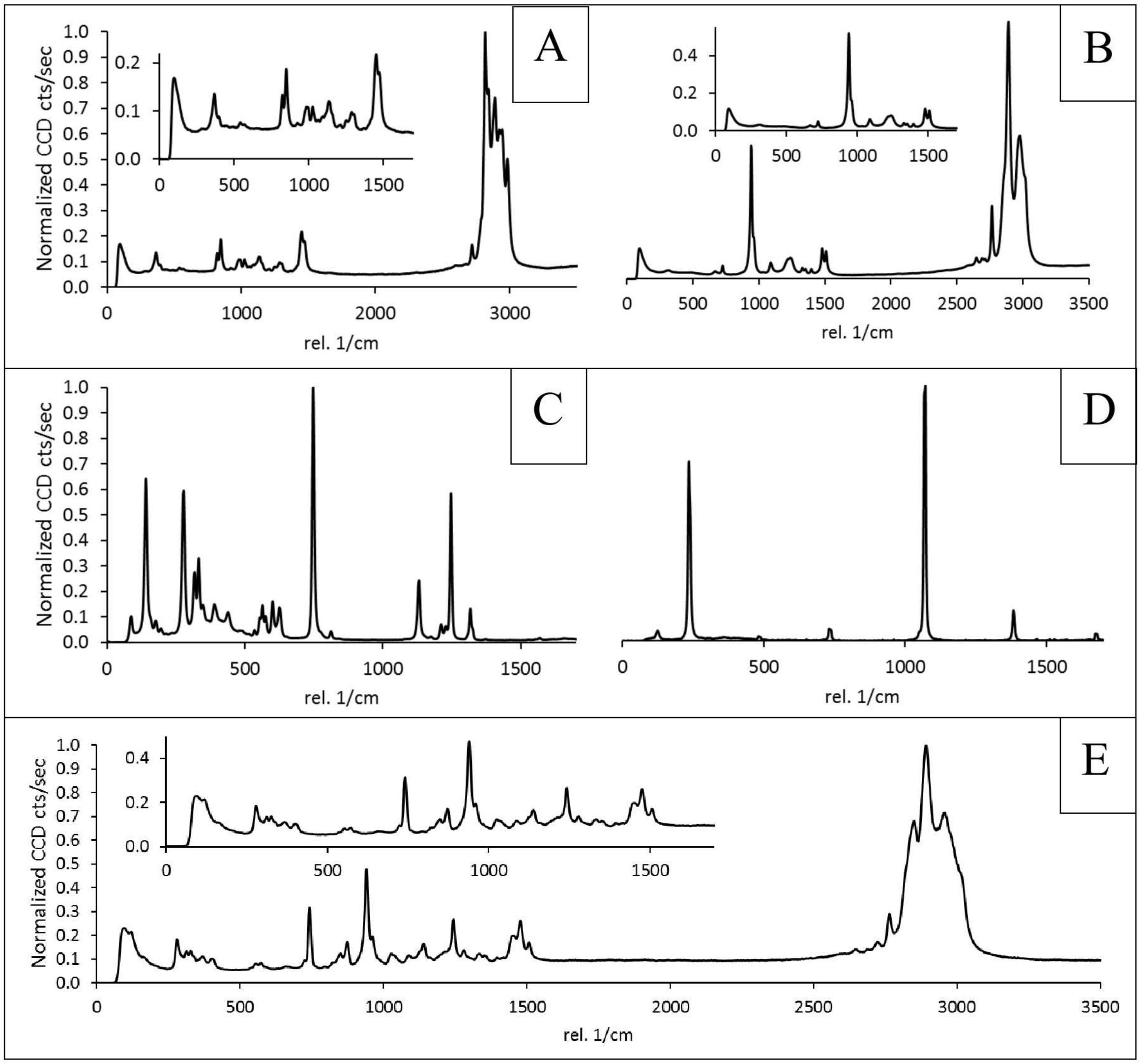

Figure S3: Spectra of components composing the electrolyte including A.) DME, B.) DOL, C.) Osilla LiTFSI, D.) $LiNO_3$, and E.) the entire electrolyte of 1:1 DME: DOL, 1 M LiTFSI, and 0.25 M $LiNO_3$. A, B, and E contain insets showing the region of wave numbers with the most Raman activity above the full spectrum with the C-H peaks in the 3000 cm^{-1} range. All materials were kept under argon in quartz cuvettes.

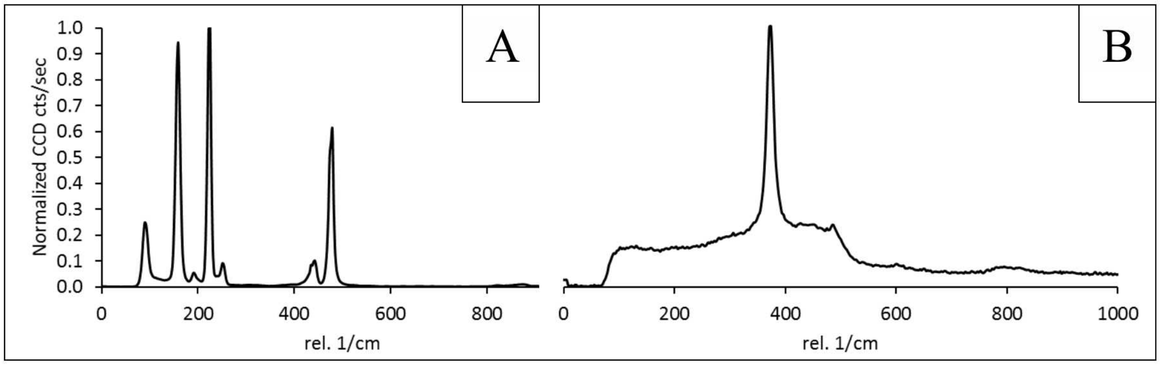

Figure S4: Raman spectra for A.) S_8 in air and B.) Li_2S under argon using a laser power of 8 mW, 30 seconds integration time, and 10 accumulations.

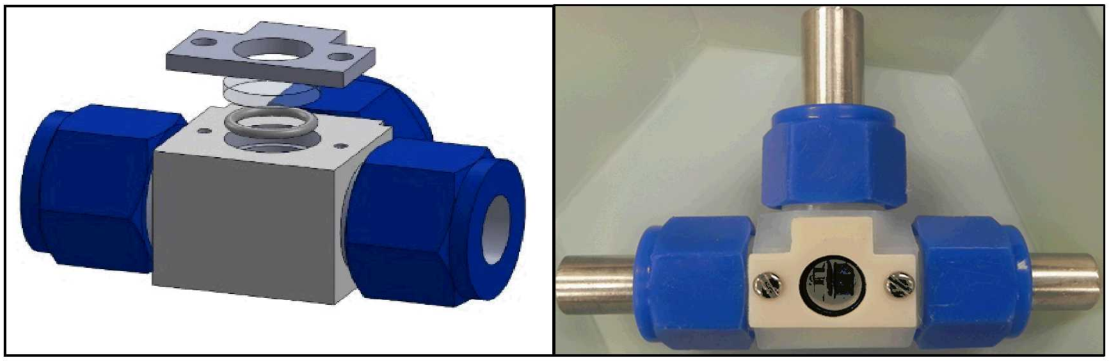

Figure S5: *In situ* Raman T-cell setup.

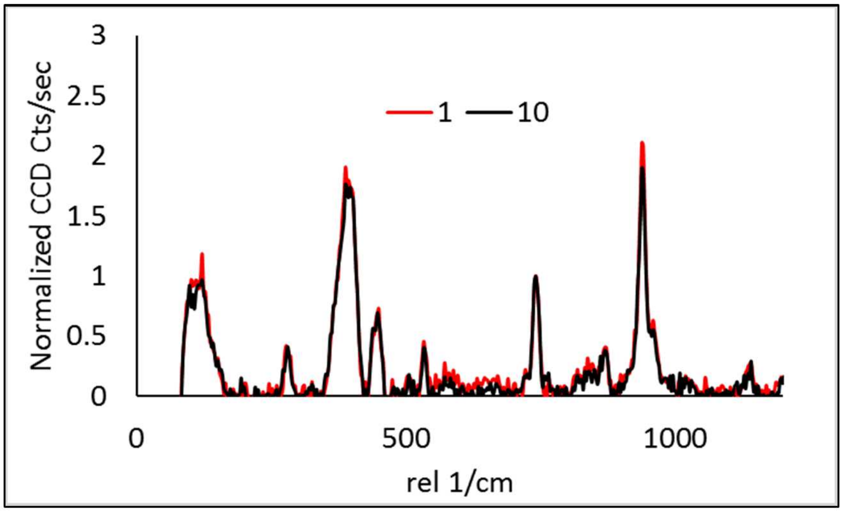

Figure S6: Raman spectra of a Li_2S_8 standard showing the spectrum after the first (red) 30 second accumulation and the 10th (black) using 8 mW power and 10 accumulations of 30 seconds integration time.

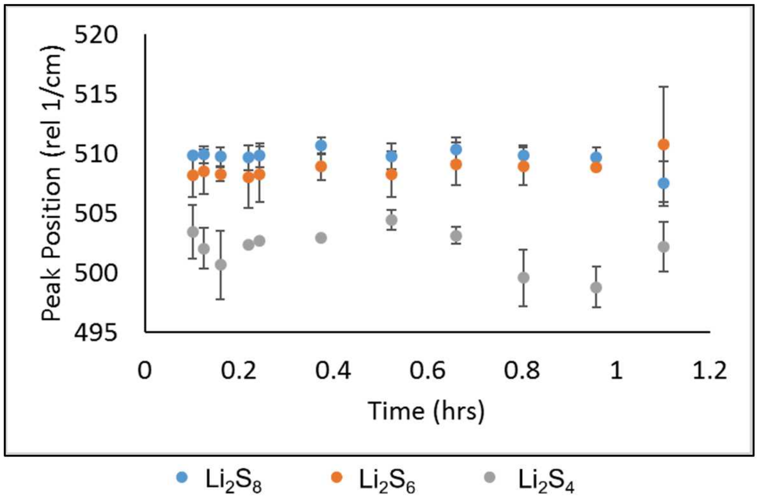

Figure S7: Stability study of polysulfide standards under argon. The peak position in the 510 cm^{-1} range was monitored for the Li_2S_8, Li_2S_6, and Li_2S_4 standards over a week period.

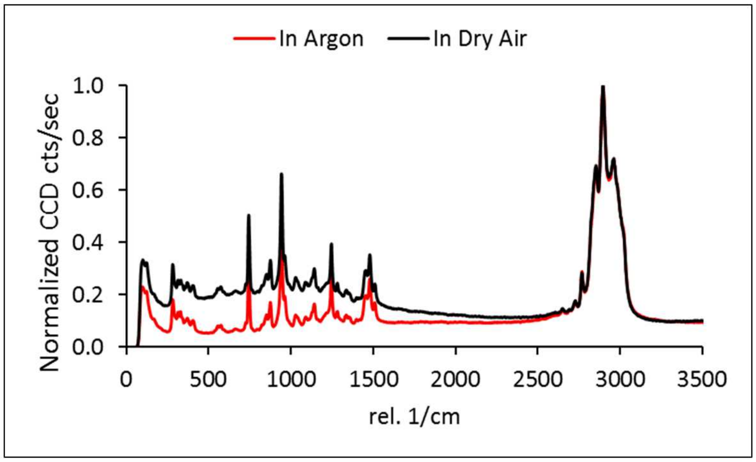

Figure S8: Difference in fluorescence background when electrolyte was under argon vs. under dry air.

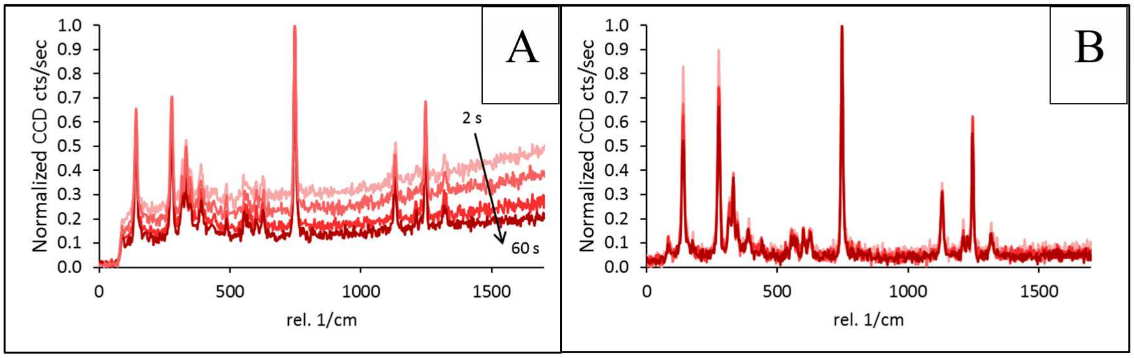

Figure S9: LiTFSI time study in A.) dry air and B.) argon from 2 seconds illumination time to 60 seconds illumination time showing the effect of photo-bleaching at a power of 8 mW.

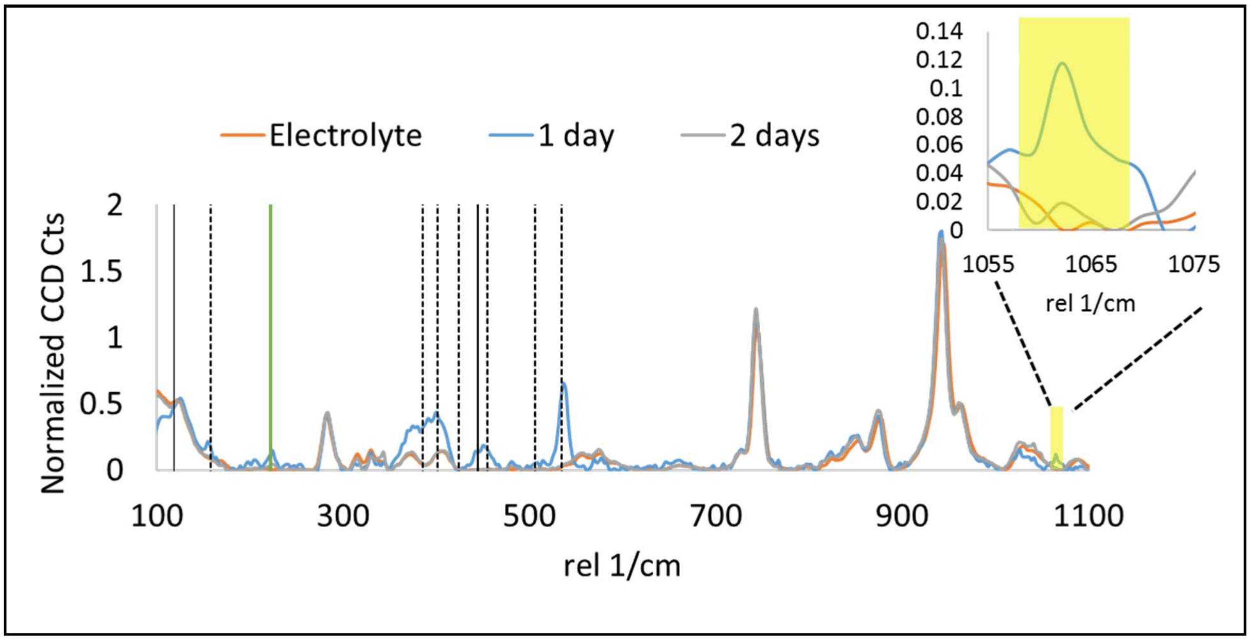

Figure S10: Polysulfides exposed to air 1 and 2 days after being synthesized (blue and grey). The electrolyte sealed under argon is shown for comparison of peaks (orange). An inset of the dithionite anion, $S_2O_4^{2-}$, is shown in the top right. Dotted and solid lines correspond to polysulfide monoanions and dianions from the literature[12, 24] respectively. The background of all spectra has been removed, but electrolyte peaks are still present.

Figure S11: Difference in coloration of the Li_2S_8, Li_2S_6, and Li_2S_4 standards in argon

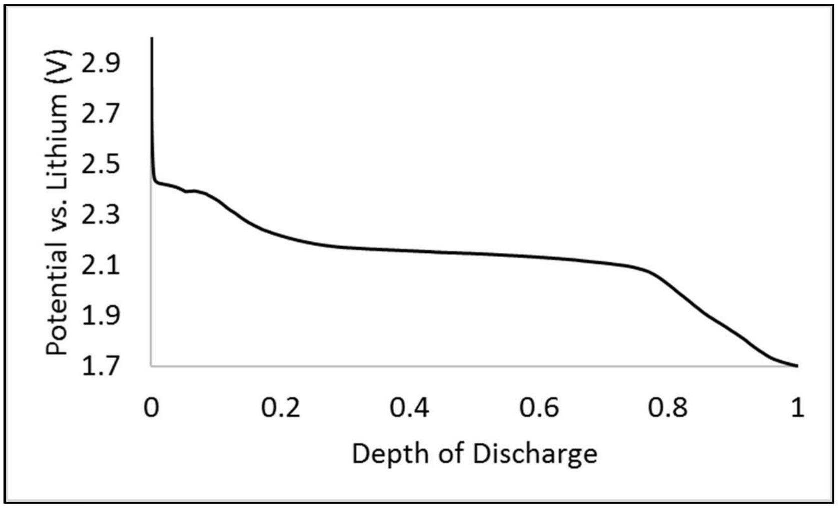

Figure S12: Normal, constant current discharge of a T-cell at

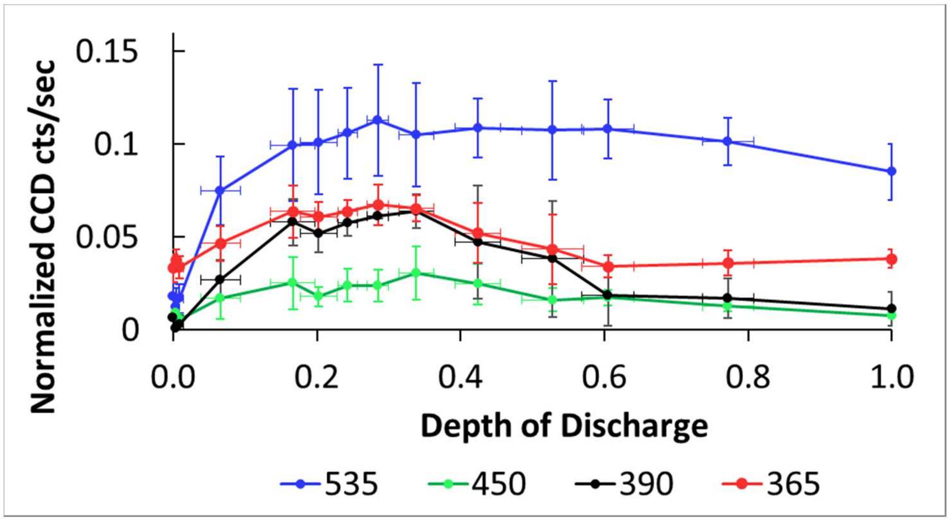

Figure S13: Normalized intensity as a function of depth of discharge for the *in situ* cell.

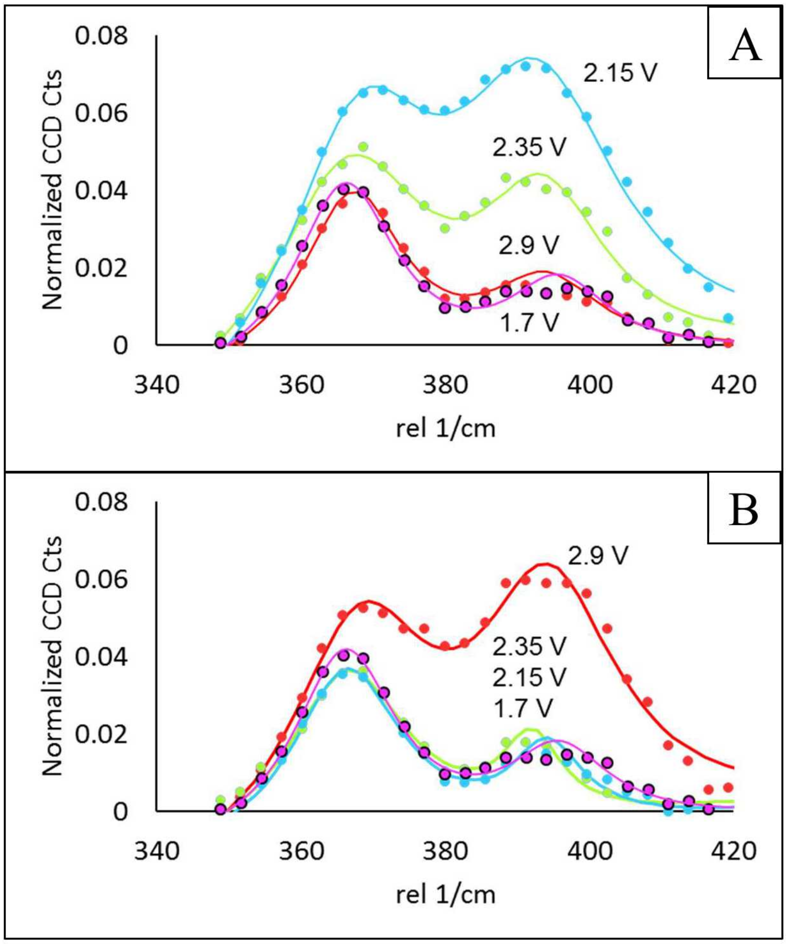

Figure S14: Representative fits of the peaks located at approximately 365 and 390 cm^{-1} during A.) discharge and B.) charge. This shows how the peaks shift and broaden during discharge. Colors are consistent with previous *in situ* spectra for each voltage.