

Infrared spectral enhancement of an electrochromic cell by water removal

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Abstract

The spectroscopic properties of an electrochromic cell in the mid-infrared and near-infrared regions have been investigated. Absorption modes due to moisture were found to hinder the performance of the device by absorbing in the frequency range 3000 cm^{-1} to 4000 cm^{-1} . A method was developed to remove water from the cell by paying careful attention to the creation of the electrolyte gel. This electrolyte gel creation process was completed in an argon environment with low moisture content. The experimenters have had great success controlling the mid-infrared region of the cell by removing water from the electrolyte gel and preventing cell contact with air. The opaque state of our device showed 20% to 25% reflectance at 0 V applied potential over a range of 2000 cm^{-1} to 6000 cm^{-1} . At -1 V the device was maximally reflective at $R=90\%$ from 2000 cm^{-1} to 6000 cm^{-1} with a C-H absorption mode lowering reflectance to 65% at 3000 cm^{-1} . The methods and devices used to create and protect a poly[3,4-(2,2-dimethylpropylene-dioxy)thiophene] (PProDOT-Me₂) based electrochromic cell are presented.

Introduction

Conjugated polymers with non-degenerate ground states are ideal electrochromic materials. These materials operate on the principle that a doped polymer exhibits spectral differences from the polymer in an undoped state. This property of non-degenerate ground state polymers is of significant importance; it provides a basis for controlling the spectral properties of materials. In particular, it is the absorption spectrum of an electrochromic device that is dynamic and predictably controlled. The doping is performed in real-time by attracting anions to the polymer, thereby causing defects in the conjugated polymer chain. In practice, two electrodes deposited with the polymer and held at a constant potential difference facilitate this ion attraction.

Electrochromic devices based on poly[3,4-(2,2-dimethylpropylene-dioxy)thiophene] (PProDOT-Me₂) have gained recent attention. These devices have shown large reflectance changes in the frequency region 2000 cm⁻¹ to 14000 cm⁻¹ when a potential is applied. Despite having desirable near-infrared properties, PProDOT-Me₂ based electrochromic cells have been found to contain two undesirable absorption bands. These absorptions occur near 3000 cm⁻¹ and 3500 cm⁻¹ and are due to a carbon-hydrogen (C-H) stretching mode [1] and an oxygen-hydrogen (O-H) stretching mode [2] respectively. The polymer is not responsible for all of these unwanted absorption modes. Rather, it is the electrolyte gel required during cell construction that is absorbing these important frequencies [3]. The C-H mode is due to chemicals in the electrolyte gel, and can only be removed by using a different gel. We set out to minimize its absorption by carefully controlling the thickness of the electrolyte gel on the electrode. The O-H mode is introduced when the electrolyte gel is contaminated with moisture from the environment. With careful preparation, we aimed to remove the water from our electrochromic cell and show an increase in the performance of the device between 3000 cm⁻¹ and 4000 cm⁻¹. This performance increase would come in the form of increased changes in reflectance between the doped and neutral states of the polymer. Extending the abilities of the electrochromic device in this region will allow for possible commercial use in the low frequency near-infrared.

Equipment and Experiment

Our electrochromic cell is based on a layered structure of electrodes. We require only that the polymer experience a potential difference, so the only necessary component is polymer-deposited electrodes. A top polymer provides a measurable surface, while a bottom electrode is used as an ion

storage device when the top electrode is in a transparent state. Unfortunately, the anions have a hard time migrating unless given an electrolyte as a medium. In the lab, the entire device must be covered in electrolyte to facilitate this migration. Our electrolyte gel is made from a mixture of four chemicals: poly(methyl methacrylate) (PMMA), acetonitrile (ACN), propylene carbonate (PC), and $\text{Li}[\text{N}(\text{CF}_3\text{SO}_2)_2]$. The ACN acts as a solvent and evaporates from the gel relatively quickly. Letting the gel mix for several hours as the ACN evaporates minimizes the influence of ACN on the gel spectrum. Creation of the gel was performed within an argon glove box. The gel was mixed for roughly 3-4 hours in the argon environment before it was stored. Use of this gel was restricted to the argon environment to ensure that no moisture was ever in contact with it. The argon environment was also maintained at a very low oxygen concentration, from 1.5 to 2 ppm at most times and never rising above 4 ppm.

A schematic for the electrochromic cell is shown in Fig. 1. This layered structure requires a material separating the electrodes that is both insulating and capable of permitting the migration of anions. We have used a porous paper roughly 150 μm thick for this purpose.

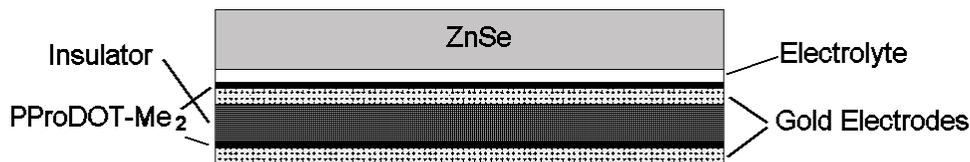


FIG. 1. The layered structure of our electrochromic cell (not to scale). The thickness of each layer from top to bottom is: 2 mm ZnSe, 125 μm electrolyte, 200 nm polymer, 75 μm electrode, 150 μm insulating paper, 200 nm polymer, 75 μm electrode.

The top electrode is covered with a thin gel layer and cut with a razor blade to allow the flow of ions. This same slit electrode must be covered to prevent exposure in the environment. We decided on a 2 mm thick Zinc Selenide (ZnSe) window to serve as the protective cover. The transmittance of the ZnSe window is ideal for infrared measurements at wavenumbers higher than 600 cm^{-1} . Below the ZnSe window and the layer of electrolyte gel are two polymer-deposited gold electrodes separated by gel-soaked paper. The polymer was deposited using a potentiostatic technique [4]. In this technique, the polymer is collected on an electrode by a potential applied across the monomer solution. We have used this method to grow polymer surfaces roughly 200 nm in thickness. Construction of the separate layers was performed entirely within the argon environment to keep moisture out and to minimize exposure of the polymer to oxygen.

An airtight reflectance stage was designed to hold the electrochromic cell and is shown in Fig. 2. A frame of aluminum surrounds the sample holder and attaches to an existing translation stage. The translation stage provides three degrees of freedom for the sample. Two rotational degrees of freedom are provided by a vertical and horizontal axis running through the center of the sample holder. These five degrees of freedom allow for simple control of the electrochromic cell in all desired positions and orientations. This control is necessary when aligning the sample inside our measurement device for maximum detector signal.

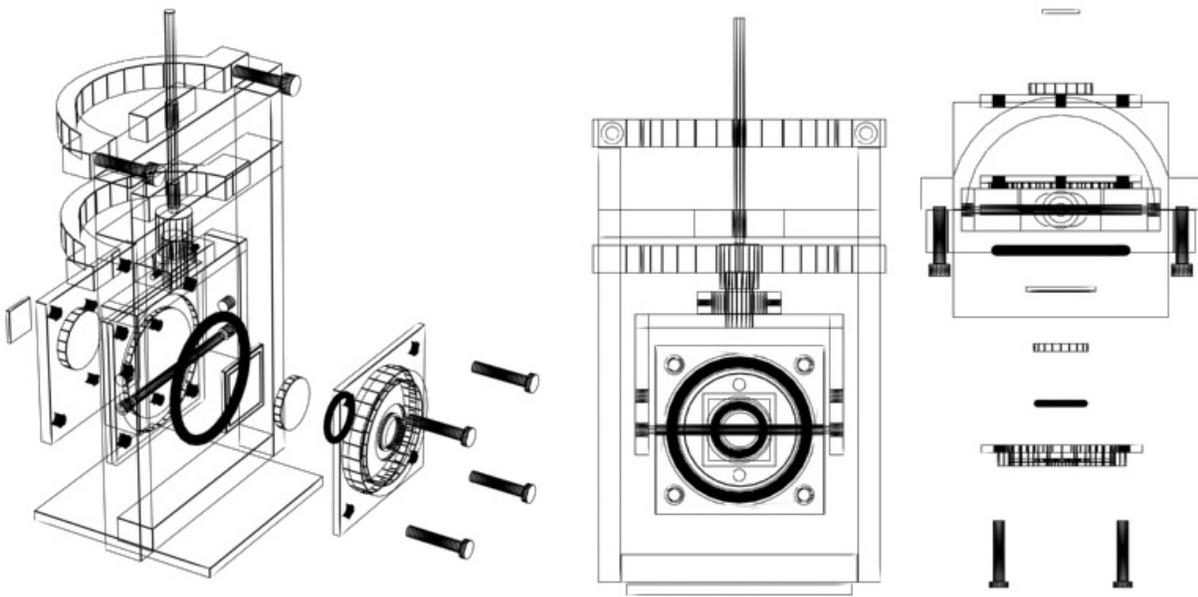


FIG. 2. The reflectance stage designed for measurement of the electrochromic cell , shown in perspective, front, and top views.

A sandwich structure can be seen in the perspective view of the sample holder. A top facing front panel holds an inner O-ring in contact with the ZnSe window, followed by the electrochromic polymer layers and gold electrodes. The base of the electrodes is supported by a thin rubber sheet and a back facing panel holding a larger O-ring, which seals the chamber. These O-rings prevent air leaks and keep the sample from being exposed to moisture and oxygen. Behind the back facing panel is a gold reference mirror and a final backwards-facing aperture. Two leads were brought into the sealed chamber to contact the electrodes through epoxy-sealed holes in the back plate. Adding Mylar rings to the sample holder between the ZnSe window and the top electrode accommodates control of electrolyte gel thickness. The control of gel thickness allows for minimization of its spectral effects when the Mylar size is minimized. This particular design puts the components of the cell under pressure. Pressure on the inside of the device is maintained at one atmosphere, even when in a

vacuum. Because of this, the cell must be held with a pressure greater than 15 lb/in² by four screws on the periphery.

Fourier-Transform Infrared (FTIR) spectroscopy techniques were used to measure transmittance and reflectance spectra. This technique resolves radiation intensity as a function of radiation frequency using an interferometer. A Bruker 113v FTIR spectrometer, which allows for taking spectra measurements in a vacuum, was the principal data-taking device. The reflectance stage and frame described above fit comfortably into a reflectance chamber within the Bruker. A hot element radiating in the infrared is focused onto the sample and reflected at near-normal incidence to a detector, where the spectra are measured. Transmission measurements were made of the electrolyte gel using a similar technique. Instead of reflecting the radiation off the sample, the radiation is allowed to pass through the sample.

Using this FTIR spectrometer and the airtight sample holder, we have measured several infrared spectra of electrolyte gel transmittance. The electrolyte created in a large argon glove box was then compared to the electrolyte created in a wet environment (in air). We have also measured the electrochromic device at several potentials to see possible increases in reflectance near 3000 cm⁻¹ and 3500 cm⁻¹. This device was made completely in a dry argon box using the gel created in the same environment.

Results

Transmittance measurements of the gel electrolyte are shown in Fig. 3. After measuring the protected gel we opened the sample holder to the air for one minute and then measured again. The absorbing O-H mode in the gel can be seen clearly in the spectrum of the exposed electrolyte at 3500 cm⁻¹. This mode was removed almost completely, as can be seen in the spectrum of the protected electrolyte, demonstrating that our process successfully prevented moisture from entering the gel.

The gel was measured between two ZnSe windows separated by a 25 μm Mylar spacer. The ZnSe windows are partially reflective and partially transparent, so they act in parallel as if they were a Fabry-Perot interferometer. This behavior is undesired but unavoidable for a thickness of this size (on the order of the wavelength of infrared radiation). Having a Fabry-Perot interferometer in the beam path creates fringes, which manifest themselves as sinusoidal modulations of the spectra. Frequencies matching closely with the fringe frequency were suppressed from the Fourier transform of the spectra.

Thus, the data shown in Fig. 3 have been modified to eliminate any fringe effects caused by the ZnSe windows.

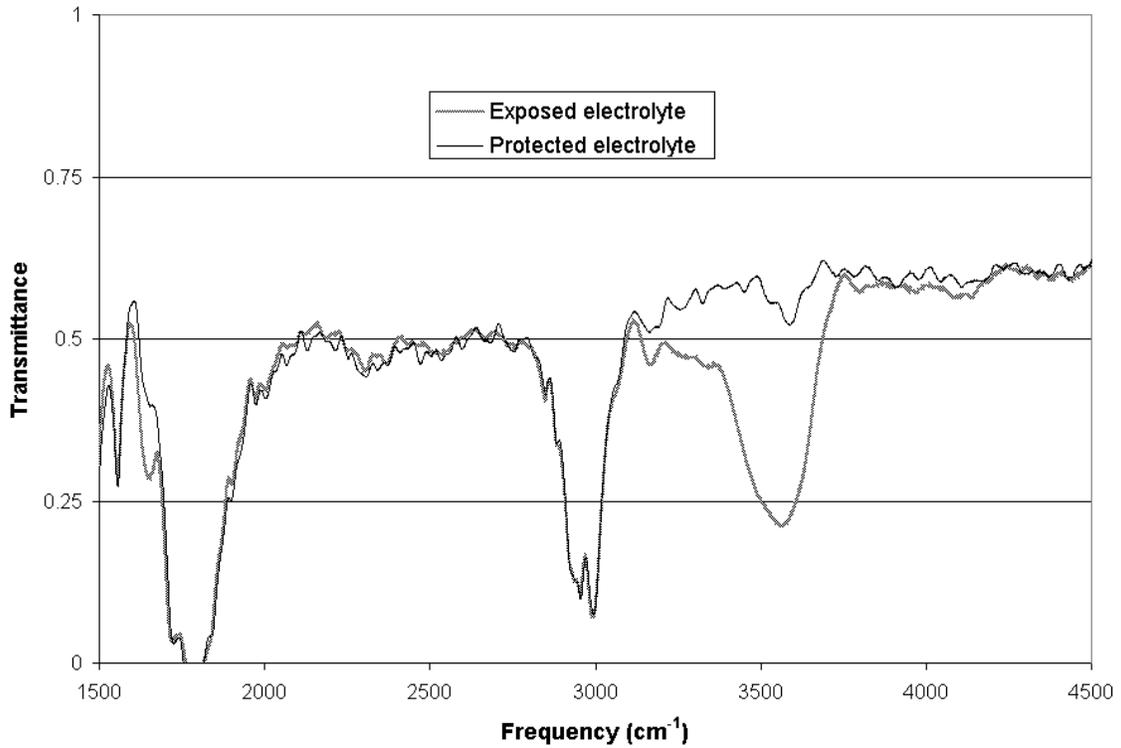


FIG. 3. Transmittance spectra of the 25 μm electrolyte gel, before and after exposure to air.

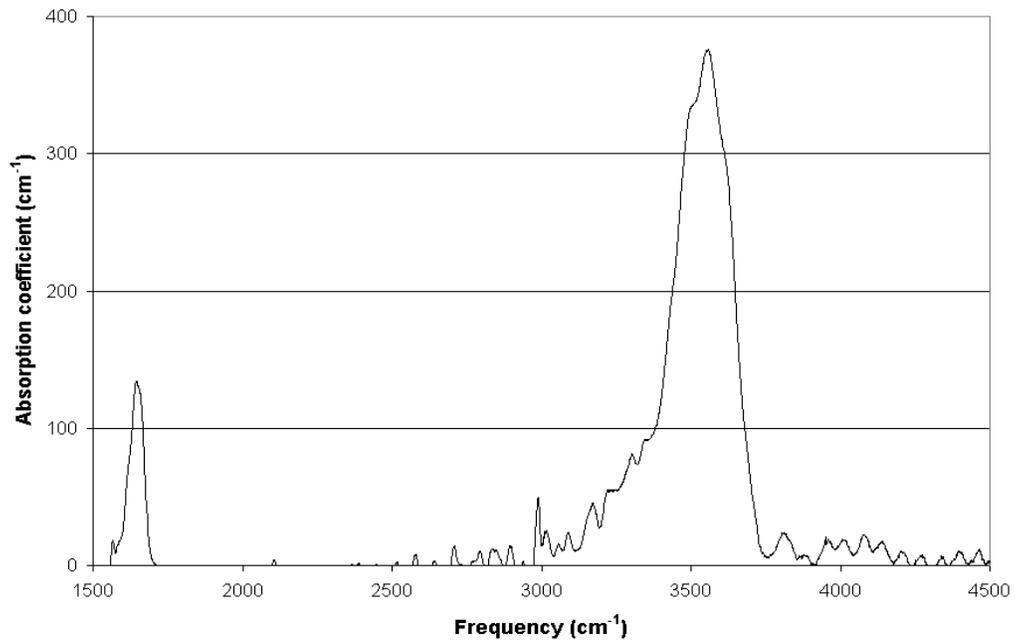


FIG. 4. Absorption coefficient of water contained within the gel electrolyte, calculated using the contaminated and non-contaminated gel transmittance spectra.

The ratio of these two spectra was calculated and used to verify that the O-H mode contamination was due to water as claimed in previous studies [3]. We have used the spectral differences to infer the absorption coefficient plot for the contaminant. Figure 4 is a plot of the absorption coefficient α for

the contaminant. This coefficient was calculated as $\alpha \cong -\frac{1}{L} \ln\left(\frac{T_c}{T_p}\right)$, where T_c and T_p are the transmittance of the contaminated gel and protected gel, respectively, and L is the thickness of the gel (25 μm). Water absorption bands can be seen clearly. The large peak near 3500 cm^{-1} (symmetric and antisymmetric stretch) and the smaller one at 1639 cm^{-1} (symmetric bend) are characteristic of a water absorption spectrum [2]. This result confirms that moisture is the contaminant, as predicted.

Using the protected electrolyte gel, we constructed an electrochromic cell to test in the reflectance stage. This new electrochromic cell showed much greater reflectance changes in the 3500 cm^{-1} range compared to electrochromic cells built with moisture contaminated gel. Also, the spectra of our new cell have only small C-H absorptions; this is due to our ability to control and minimize the gel thickness.

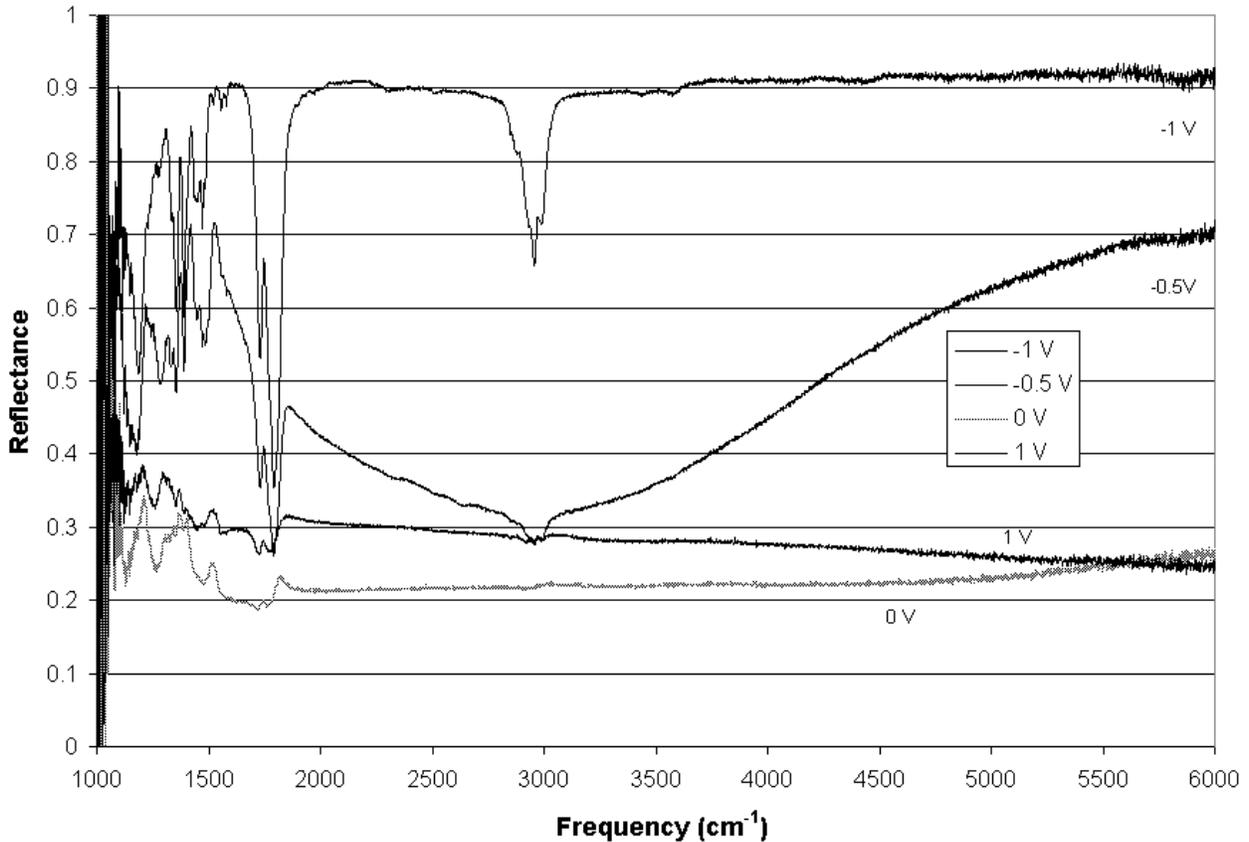


FIG. 5. Changes in reflectance for a 200 nm thick PProDOT-Me₂ electrochromic cell with 125 μm electrolyte thickness at various potentials.

Reflectance spectra were taken as the potential across the sample was changed from -1.0 V to $+1.0$ V, as shown in Fig. 5. The reflectance is maximized when -1 V is applied, so voltages approaching -1.5 V are not necessary. The maximum opaque and transparent states of the polymer differ by as much as 70% ($\Delta R = 70\%$) at 2200 cm^{-1} . The opaque state shows 20% to 25% reflectance at 0 V from 2000 cm^{-1} to 6000 cm^{-1} . At -1 V the device was maximally reflective at $R \approx 90\%$ between 2000 cm^{-1} and 6000 cm^{-1} with a C-H absorption mode lowering reflectance to 65% at 3000 cm^{-1} .

Switching times for potential changes were extremely slow; on the order of one to two hours for a full switch. Times required for the cell to come to optical equilibrium are shown in Table I. The characteristic switching time for this cell was 60 to 120 minutes. Long switching times are thought to be a consequence of thin gel layers and high pressures on the electrodes. This belief can be understood if one notices that the thin cuts in the upper electrode squeeze together when under pressure. A few simple tests were performed, showing that the device was capable of a full switch in 1.5 seconds when not under pressure. This result would seem to suggest further study into the possibilities of quick switching in a airtight sample holder.

TABLE I. Switching times for the electrochromic device.

	Minutes
-1 V to -0.5 V	40 to 60
-0.5 V to 0 V	40 to 60
0 V to 1 V	45 to 70
1 V to -1.5 V	60 to 120

Discussion

We have seen that gel electrolyte causes unwanted absorption in the infrared due to water contamination and C-H bonds in the electrolyte. Removing moisture increased the capabilities of the electrochromic cell in the region near 3500 cm^{-1} . This water contamination occurred extremely quickly. After one full minute of exposure, the gel showed as much water absorption as a cell that had been constructed entirely in a moist environment [3]. Minimizing the effects of the C-H bonds was demonstrated by using very thin electrolyte layers; however, these thin electrolyte layers were shown to dramatically increase the switching time when under pressure. This is an undesirable result that may be improved upon with further research. Some possible ways to attack this problem include using

larger, more frequent cuts in the upper polymer. Designing a new sample holder that does not require large pressures on the top electrode may also decrease the switching time considerably.

Reflectance changes in the polymer were checked several times to make sure they were repeatable. Due to time constraints, only a few (4 to 5) potential switches were completed. Each switch showed that consistent results were possible, as the switching times remained relatively constant over four double potential switches (−1.5 V to +1V and back four times). Further research is possible regarding tests of this nature. We expect that the results of such an investigation will show that the lifetime of the cell is increased over older methods due to isolation of the cell layers from the environment. Previous methods for holding the cell have allowed the gel to dry and become ineffective as the contents evaporate.

References

[1] Koji Nakanishi and Philippa H. Solomon, Infrared Absorption Spectroscopy, 2nd ed. (Holden-Day, San Francisco, 1977), p. 59.

[2] Colin N. Banwell and Elaine McNash, Fundamentals of Molecular Spectroscopy, 4th ed. (McGraw-Hill, London, 1994), p.72.

[3] J. Hwang, Ph.D. thesis, University of Florida, 2001.

[4] D. M Welsh, A. Kumar, E. W. Meijer, and J. R. Reynolds, *Adv. Matter.* **11**, 1379 (1999).