Electropolymerization of an Electrochromic Device Based on PEDOT

Introduction

Electrochromic devices are devices that show a reversible change in color, or optical density, with a change in voltage or electric potential.\textsuperscript{1,2} Such devices are used, for example, in sun windows that can be darkened to help keep a room cool, or in variable reflectance mirrors in cars. Other potential applications include display panels and camouflage materials. Desirable attributes for an electrochromic device include complete transparency and lack of color in the “off” state, and very dark color in the “on” state. Low switching voltage is also important. In addition, an optimal system should show hysteresis. That is, you should be able to take the system to a positive voltage to switch the color. If the voltage is then reduced to zero, the color should remain. The color should only switch back when the device is taken to a negative voltage. Similarly this new color should remain until the device is again taken to a positive voltage. In this way, the device does not need to be powered at all times and the total power consumption is reduced.

Electrochromic devices can be made from either organic or inorganic material, as long as the material has multiple stable redox states that have different UV-visible-IR absorption bands. The advantage of inorganic based electrochromics is that they are generally much more stable in sunlight and have longer lifetimes. The disadvantage of inorganic based devices is that they are much more expensive to produce than their organic counterparts. Similarly, the advantage of organic based devices is that they are inexpensive and easy to produce, while the disadvantage is a short operating lifetime.

Here, you will create an organic electrochromic device from 3,4-ethylenedioxythiophene (EDOT). EDOT can be polymerized electrochemically to form the semiconducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT).

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\text{EDOT} & \xrightarrow{\text{electrochemical polymerization}} \text{PEDOT} \\
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Electropolymerization is a very easy way to produce electrochromic materials as the polymer is formed directly on the same electrode that will be used to switch its color. Despite its ease, electropolymerization is not a good way to make conducting or semiconducting polymers for LED-type applications because the polymer chains that form are often short and are highly aggregated. As a result, the resistance of these polymers is high and it is hard to get large amounts of current through the
material. For electrochromic applications, however, very little current flows (only enough to oxidize or reduce the polymer), and so electropolymerized materials behave very well.

In this laboratory, you will produce a PEDOT film by electropolymerization. You will then explore how the film can be oxidized/reduced and explore how the absorption spectrum changes at different voltages. All of this work will be done on a sample held in a solution of electrolyte. The liquid electrolyte is not terribly practical for device applications, so in the next part of the lab, you will create a gel electrolyte and fabricate a free standing device. Finally, you will determine the color of your device in the dark state using the CIE gun.

Procedure

Overview

Day 1 Deposit PEDOT films. Start dissolving the polymer electrolyte.
Day 2 Using the liquid cell, collect CV data and measure absorption as a function of voltage. Make the gel for your device.
Day 3 Measure color change with voltage for the gel cell. Determine the CIE coordinates of your device.

Electrochemical Polymerization

1. Prepare 0.1 M LiClO$_4$ in propylene carbonate (≈10 ml). Add the required amount of 3,4-ethylenedioxythiophene (EDOT) monomer to make a solution that is at most 0.02 M (20 µl or less). Add ~2 ml of this solution to a cuvette. Bubble the solution with N$_2$ or Ar for approximately five minutes prior to use to remove oxygen. Stir with the bubbling needle/pipette to ensure that the solution is homogeneous. Also prepare 0.1 M LiClO$_4$ in propylene carbonate (≈10 ml) to use as your electrolyte solution, you will use this solution when switching your films.
2. Get a number of ITO-coated glass slides and use a handheld multimeter to determine which side is ITO coated; put a small scratch in the corner of the ITO side on each slide. Clean the ITO surface by sonicating in soap and water, then acetone, and then ethanol, ensuring the slide is clean and streakfree.
3. To set up your electrochemical cell, position the wires equidistant across from the ITO side of the glass slide in a plastic cuvette. Make sure the wire runs the full length of the ITO substrate and that the cuvette is filled all the way with solution. Attach the counter electrode (red) to the platinum wire, and the working electrode (green) to the ITO glass. Ensure that the wires are not touching each other, or touching the ITO glass. Also include a silver wire as your reference electrode (white). There is a teflon cap that you can use to hold the ITO and both wires. Note that the plastic cuvettes are slightly
soluble in solvent you are using, so make sure you do not spill solvent on the outside of the cuvette or it will get sticky!

4. Open Powersuite on the computer. To deposit a film at constant voltage, then click tools then virtual potentiostat. Connect to instrument (insuring that it is turned on first) adjust the voltage to 1.8 V. (if you have deposition problems, it is possible that the reference electrode has oxidized. Try polishing it using the polish on the west wall). Let this polymerization go for about three seconds. You can apply the voltage with the “enable” button. Don’t worry about this sample, because it will be of low quality due to impurities in the propylene carbonate. After deposition, discard this sample and polymerize a second film from the same solution. The first reaction will get rid of reactive species in the solution and your second film should be of much higher quality. Be careful not to make your films too thick—the color you see will be that of the oxidized polymer, which is in the bleached state. After reduction to the dark state, a thick film will be too dark for absorption measurements and will not switch well. A more dilute EDOT solution will result in slower film growth and will give you better control of film thickness. Be aware that it is possible to use up all the monomer in your solution—at this point, you will not be able to deposit a film! Try to make films of two different thicknesses (polymerization times of approximately 10 and 30 seconds).

Note that the deposited film is fragile: be careful when handling the substrates as the film is quite easy to scratch off. DO NOT PULL YOUR FILMS UP THROUGH THE CAP, TAKE THE CAP OFF THEN REMOVE THE FILM FROM THE CUVETTE. Additionally, the films perform best on the day they are made. If you have time on the same day, collect CV data (it might even be preferable to collect data on each film as they’re made). Finally, store your films in an electrolyte solution.

Film Testing

1. Run cyclic voltammetry (CV) to test the film. Rinse the slide with fresh electrolyte to remove unpolymerized monomer. Insert the slide into a cuvette with fresh electrolyte containing no monomer. Again, use platinum as your counter electrode and a silver wire as the reference electrode. Click the “experiment properties” icon to set up the CV. Scan from 1.5 V to –1.2 V and back to 1.5 V at a scan rate of 100–200 mV · s⁻¹. You should observe color change of the polymer film. Save this data to make a correlation between your CV and your absorbance.

2. Measure the absorbance while applying various potentials. Apply the various potentials for approximately 5 seconds to switch the films. Measure the absorbance from 400 to 1600 nm beginning at 1400 mV. Leave the film connected to the potentiostat so that you could decrease the potential in 200-mV increments without removing the sample from the UV-vis spectrophotometer. Continue obtaining spectra until little or no change is observed between spectra. Note that you will need to turn on the IR detector in order to collect data at wavelengths longer than 800 nm.
3. Compare thick films with thin films, both in terms of the optical density and positions of the absorption peaks, and in terms of the switching voltages.

4. Once you are done with the films switch them to the blue state and store them like this. DO NOT THROW AWAY ITO. If there are films that you do not use for your device, clean the film off the ITO by rubbing the ITO with a gloved hand and soapy water.

Device Fabrication

1. Prepare the gel electrolyte casting solution by mixing poly(methyl methacrylate) (MW = 120000) (500 mg), propylene carbonate (2.5 ml), and acetonitrile (3 ml). Then add lithium tetrafluoroborate (100 mg) and mix the solution overnight. You can equivalently use LiPF$_6$. Heat the gel to drive off the solvent; it is okay if it boils. The solution will turn a brown color and should be viscous.

2. Before you make your device, you can pull vacuum on the solution to make the gel more viscous. Cast the viscous gel across the entire polymer electrode, making sure that there are no air bubbles. Gently place the conductive side of a second piece of ITO onto the gel. The ITO slides should not touch each other—DO NOT press the sandwich together!

3. Use epoxy to seal the sides and make the device more robust. Wrap a small piece of tape around each end of your device to hold together back while applying epoxy.

4. Attach the reference and counter (red and white) electrodes to the non-polymer coated ITO glass slide. Attach the working (green) electrode to the polymer coated ITO glass. Color change should be observed with voltage change from $-2.0 \text{ V}$ (colored) to 2.0 V (bleached). Collect CV data and some absorption data at different voltages and compare to the data you collected with the solution cell.

5. Using the CIE gun and the outside light setting of the box, determine the CIE coordinates of your device in the dark (reduced) state. If your device did not work well, just use a dark (reduced) film that is not part of a device. You will need to use the close-up lens to focus on the device only. You can ignore the first number from the CIE gun, which relates to saturation or hue. The second two numbers should be the x and y chromaticity coordinates (related to red and green fractions). Calculate CIE coordinates from your absorption spectra using the Labview program CIEfit and compare to those obtained from the CIE gun. Save your UV-Vis data as tab-delimited text files to use with the LabView program. If the optical density of your sample is low, multiply the whole spectrum by a constant to get the peak O.D. to be greater than 1 in the dark state. This will make your colors appear more
saturated and less white. Use the same constant for all spectra that you analyze and look at both
dark-state and light-state films.

Some Thought Questions

1. How does the electropolymerization process occur? What chemical reaction is occurring? Why must
   it be performed at a positive, rather than a negative bias? What impurities are you trying to get rid of
   in the first polymerization?
2. Why does the thickness of the polymer film matter for device performance? How might you measure
   the film thickness?
3. How many peaks do you see in the cyclic voltammetry for the PEDOT film? What chemical process is
   each peak associated with? Can PEDOT be both oxidized and reduced from its neutral state?
4. PEDOT is a semiconducting polymer. As such, it has a band gap. How would you measure this band
   gap? How would changing this band gap change the functionality of the electrochromic device?
5. Why is the doped polymer a different color than the neutral polymer?
6. Do the thick films switch better or worse than the thin films? Why might this be?
7. Correlate your CV data to your absorbance data.
8. Do the CV curves look the same for the liquid cell and the gel cell? Can you explain the source of any
   differences?
9. Why should you care about the CIE coordinates of your electrochromic device?

References