Using Organic Light-Emitting Electrochemical Thin-Film Devices To Teach Materials Science

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According to the inquiry model of learning, students learn science best when they act as scientists. Developing high-tech materials gives students at varied levels the opportunity to learn science principles through an authentic experience. These experiences foster basic technical competence and problem-solving skills, which are important in a world market where these skills are required in nearly every job.

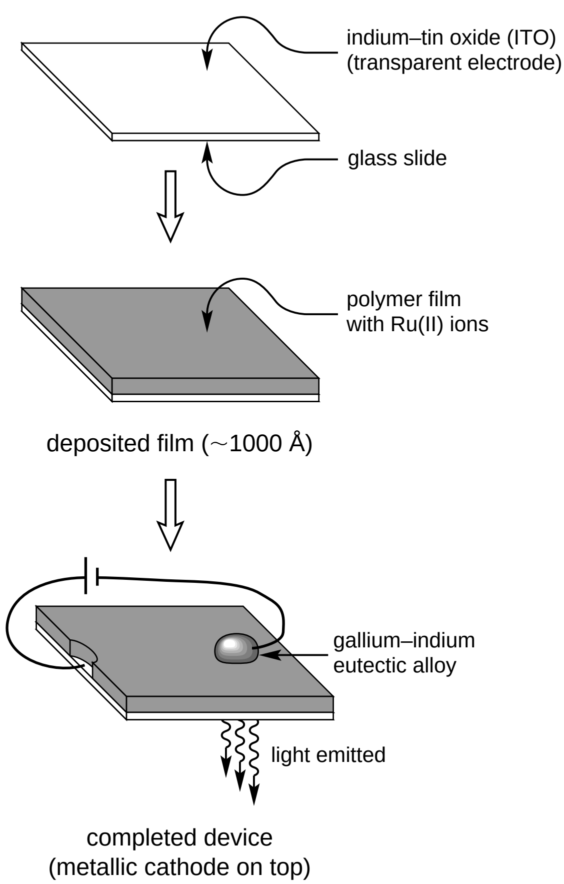

Figure 1. Device fabrication: Begin with glass slide coated with ITO. Spin-coat thin film containing $[Ru(bpy)_3]^{2+}$ and Cl^- ions embedded in polymer matrix. Place metallic Ga–In cathode on top of thin film and connect Ga–In and ITO to voltage source to emit light.

The experiments on light-emitting thin organic films described here give students the opportunity to learn about electrochemistry, spectroscopy, the microscopic structure of the solid state, and basic circuits. These experiments have been piloted in high school chemistry courses (Merrimack), university materials science laboratory courses (MIT), and with middle school and high school science teachers at various workshops. At the high school or undergraduate level, these experiments fit well within the study of solid-state behavior or electrochemistry, or in the study of materials science within a chemistry or physics class. The depth of the theory studied depends on the level of the audience. These experiments may also be adapted for upper-level undergraduate courses if quantitative measurements of voltage and light emission are explored. Experiments along these lines are described elsewhere *(1–4)*.

It is only recently that organic materials have been made to efficiently emit light *(5–7)*. Thin films of these materials, only 60 to 100 molecules thick (1000 to 1500 Å)*(8)*, can emit light that is brighter than the equivalent area on a television screen. Polymers and small molecules can be induced to emit light by passing an electric current through a liquid or solid solution. The mechanism of the electroluminescence in the case of the material used in this work involves electron hopping to transfer charge across the film and light emission by phosphorescence from the excited state created in a combination reaction.

The advantages of producing light from thin plastic films include the flexibility of the plastic, low cost of the materials involved, and the ease of manufacture. Any flat-panel display that lights up is a candidate for this technology, including such applications as display panels in automobiles, large-screen advertising displays, and backlit watch dials.

In these investigations, students make light-emitting devices by spin coating a thin film containing ruthenium(II) complex ions onto a glass slide *(2–4)*. The slide is coated with a transparent electrode on one side (Figure 1) so that the light emitted by the film is visible through the electrode and the glass. The procedure involves making solutions of ruthenium(II) complex ions (Figure 2) and a water-soluble polymer and then spin-coating a thin layer of a mixture of these onto the slide, using a spin-coater students have constructed. After drying the film to form a thin layer of ruthenium(II) complex ions embedded in the polymer matrix, droplets of a gallium–indium eutectic alloy are added to the top of the film to serve as the cathode.

As current passes through the film, the ruthenium(II) complex ions oxidize to Ru^{3+} at the anode and reduce to Ru^{+} at the cathode. Electrons are transferred toward the anode, hopping from one ruthenium complex ion to another. As electrons hop from ion center to ion center, the residences of the electrochemical species Ru^{3+} and Ru^{+} are transferred toward the center, until two unlike ions are adjacent near the middle of the film (Figure 3). At that point, Ru^{+} and Ru^{3+} combine to form a ground-state Ru^{2+} species and an excited-state Ru^{2+} species, the latter of which emits light as it returns to its spectroscopic ground state. Once the device is working, students can use their understandings of the chemical principles involved to investigate modifications to the process to improve the device performance.

To understand how the device works so students can modify it and explore its limitations, students must understand the following learning objectives:

- Electrochemistry occurs as current passes through the film.
- The film consists of ruthenium complex ions arranged in a polymer matrix.
- Light is emitted when Ru^{+} and Ru^{3+} combine to form two Ru^{2+} complex ions, one of which is in an excited state. Excited ruthenium(II) complex ions emit light via phosphorescence.

Performance outcomes include the practice of important laboratory skills. Students make solutions of polyvinyl alcohol and the ruthenium(II) complex. They build and operate circuits in the laboratory and vary the voltage or current in both the spin coater and the device. Students also take into consideration environmental conditions, such as humidity. Students establish plans for exploring the effects of modifying the device. They practice the engineering design process when investigating how these materials are developed and improved.

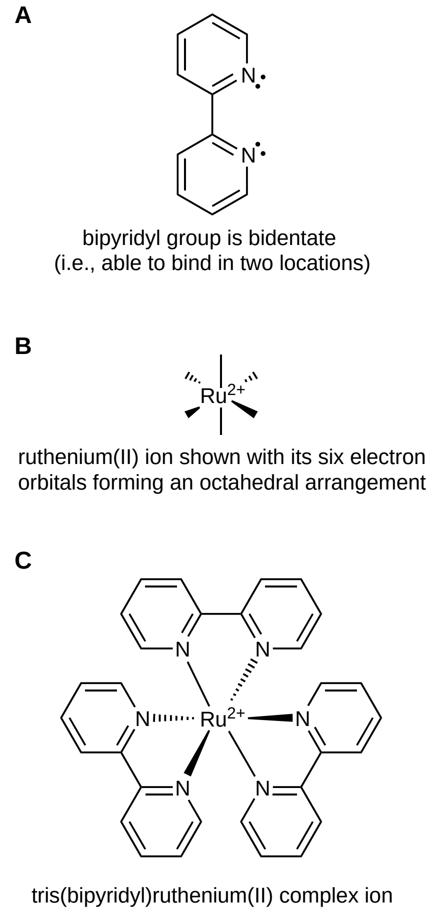

Figure 2. Structures of (A) bipyridyl group, (B) ruthenium ion showing octahedral symmetry, and (C) tris(bipyridyl)ruthenium(II) ion.

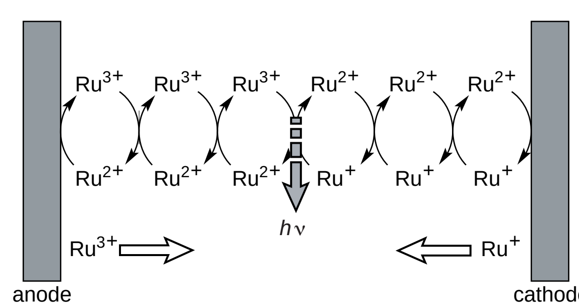

Figure 3. Electron transfer through the ruthenium film. Initially, oxidation occurs at the anode and reduction occurs at the cathode. Electrons then hop from the cathode toward the anode, while Ru centers remain in fixed locations, causing Ru^{+} and Ru^{3+} residences to move toward the center of the film. Light ($h\nu$) is emitted when a Ru^{3+} ion is adjacent to a Ru^{+} ion somewhere near the middle of the film. [Inspired by Figure 7 from Maness, et al. *(1)*]

Materials and Methods

Students are given slides precoated with the transparent indium–tin–oxide anode, plastic cover slips, ruthenium(II) chloride, polyvinyl alcohol, distilled water, gallium–indium eutectic, pipets, tweezers, cotton swabs, a hole-puncher, carpet tape, glass vials, epoxy, and gloves. They are supplied with beakers of solutions used for cleaning the slide: an ammonia-based glass-cleaning solution, distilled water, and isopropyl alcohol. They are also provided with the components necessary for assembling a spin-coater: a 5-V, 200-mA dc fan; a 6-V, 100–mA plug transformer; a 47-Ω resistor; aluminum foil; cellophane tape; and a plastic cup. They have access to a drying oven, a power supply, a multimeter, and wire leads for connecting the device.

Creating the electrochemiluminescent ruthenium-based device involves making aqueous solutions of the ruthenium(II) complex ion, $[Ru(bpy)_3]Cl_2$ (53 mg per mL of water), and of polyvinyl alcohol (30 mg per mL of water) to serve as the matrix, and then mixing the two solutions in a 1:5 volume ratio. Next, students build a simple instrument to spin a thin layer of the resulting mixture onto a glass slide precoated with the transparent electrode. Prior to spin coating, the slide is thoroughly cleaned. After the film has been dried, a drop of gallium–indium eutectic is applied to the top of the film to serve as the cathode. The device is sealed with epoxy and then lit by connecting the electrodes to a power supply. Once students have working devices, they can experiment with improving device efficiency.

Hazards

The principal chemical hazards are associated with using the ruthenium(II) chloride salt and the gallium–indium eutectic. The ruthenium salt should be treated as any transition metal salt; it is not a known carcinogen or sensitizer. The gallium–indium eutectic is a liquid metal and should be handled with care so that it does not spill. If it spills, it can be cleaned up by taking it up with a pipet and then cleaning the remainder of the spill with a cloth wet with an ammonia solution, such as glass cleaner. There are no significant hazards reported for the Ga–In eutectic.

Results and Discussion

Three processes occur during the operation of the device: charge injection at the electrodes, charge transport through the device, and light emission near the center of the device. When the power source is first turned on, electrons are injected at the metallic cathode while holes are injected at the ITO anode. Reduction occurs in ions adjacent to the cathode ($Ru^{2+} + e^- \rightarrow Ru^+$) and oxidation occurs in ions adjacent to the anode ($Ru^{2+} \rightarrow Ru^{3+} + e^-$).

The second process, charge transport, can be visualized by imagining that the device consists of an anode side and a cathode side. Initially, only Ru^{2+} complex ions are present in the bulk. After oxidation and reduction occur at the electrode surfaces, the next adjacent Ru^{2+} is oxidized or reduced by a process of electron hopping (Figure 3). However, for Ru^{2+} to change to Ru^{3+} and Ru^+ in the anode and cathode sides, respectively, counterions (Cl^- ions) must move from the cathode side to the anode side to neutralize some of the excess charge. Counterion redistribution is a slow step and contributes to a response time before the device produces light. Once the two sides contain enough oxidized and reduced species, a constant voltage steady state is achieved and, for the most part, the counterions no longer move, unlike the situation in a battery. Current now flows only by electron hopping without changing the total number of Ru^{3+} and Ru^{1+} states in each side of the device.

The third process, light emission, occurs near the center of the device. When an electron hops from a Ru^+ complex ion to a Ru^{3+} complex ion, the two ions combine to create a ground-state ion and an excited-state ion:

$$Ru^{3+} + Ru^+ \rightarrow Ru^{2+} + (Ru^{2+})^*$$

The Ru^{2+} complex ion in the excited state decays to the ground state, through phosphorescence, emitting light (red–orange, $\lambda = 630$ nm) as it does.

Several factors limit the performance of the device. One way to reduce the device response time is to synthesize special polymers with ion-conducting side groups attached along the polymer matrix. This way, counterions are channeled faster through the matrix. This approach has been shown to yield shorter response times in polymer light-emitting electrochemical cells *(9)*. It is also known that changing the size of the counterions dramatically affects response time *(10)*. A second limitation is the poor stability of the cathode and film. The devices tend to degrade at high voltages; the ruthenium oxidizes with oxygen and water vapor in the air, and the metal cathode breaks down as well. However, it has been shown that operating devices with a pulsed voltage acts to increase their stability *(3, 11)*. This is one factor that students are able to investigate.

Device performance can be measured principally by light output, duration, and response time. There are many additional factors that students may wish to explore to improve device performance. Environmental conditions, both in manufacture and in usage, affect the performance of the device. In particular, humidity affects the quality of the film. Students can vary the ratio of polymer to ruthenium complex to change the ion density, or vary the solution concentrations or spin-coater speed to change the film thickness. The temperature of the drying oven or the time of drying affects the film. The ambient temperature affects device performance. Students can explore sealants other than epoxy that might react less readily with the cathode and not dissolve the film. Students may wish to create designs in the emitted light by carving figures into the mask into which the eutectic is added. Changing the area of contact between the eutectic and the film also has an effect on device performance.

Conclusions

This laboratory provides students with an opportunity to learn about electrochemistry in the solid state and spectroscopy from the vantage point of materials science and engineering. The experiments are appropriate for high school chemistry or undergraduate chemistry or materials science courses. Students gain experience with preparing solutions and setting up and operating circuits, as well as working with the engineering design process.

Acknowledgments

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WSupplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online*.

Literature Cited

1. Maness, K. M.; Terrill, T. J.; Meyer, R. W.; Murray, R. W.; Wightman, R. M. *J. Am. Chem. Soc.* **1996,** *118,* 10609–10616.

2. Rudmann, H.; Rubner, M. F. *J. Appl. Phys.* **2001**, *90,* 4338–4345.
3. Handy, E. S.; Pal, A. J.; Rubner, M. F. *J. Am. Chem. Soc.* **1999,** *121,* 3523–3528.
4. Gao, F. G.; Bard, A. J. *J. Am. Chem. Soc.* **2000**, *122,* 7426.
5. Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51,* 913–915.
6. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. M.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347,* 539–541.
7. Pei, Q. B.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* **1995,** *269,* 1086–1088.
8. Rillema, D. P.; Jones, D. S. *J. Chem. Soc., Chem. Commun.* **1979,** 849.
9. Holzer, L.; Wenzl, F. P.; Tasch, S.; Leising, G.; Winkler, B. Dai, L.; Mau, A. W. H. *Appl. Phys. Lett.* **1999,** *75,* 2014–2016.
10. Rudmann, H.; Shimada, S.; Rubner, M. F. *J. Am. Chem. Soc.* **2002,** *124,* 4918–4921.
11. Yu, G.; Cao, Y.; Zhang, C.; Li, Y. F.; Gao, J.; Heeger, A. J. *Appl. Phys. Lett.* **1998,** *73,* 111–113.