Chem. Mater. **2005,** *17,* 4212−4217

Effect of Water Vapor on the Operation and Stability of Tris(2,2′-bipyridine)ruthenium(II)-Based Light-Emitting Electrochemical Cells

Donald L. Pile,[†] and Allen J. Bard*

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

Received February 18, 2005. Revised Manuscript Received May 31, 2005

Light-emitting electrochemical cells (LECs) based on $Ru(bpy)_3(ClO_4)_2$ are thin-film solid-state devices that typically operate at low applied voltages and show relatively high efficiencies. They suffer, however, from poor operating lifetimes. A proposed source of lifetime degradation is water in the film. Previous studies have revealed a marked difference in operation performance between cells fabricated and tested inside a drybox and those made and tested under ambient conditions. This study further characterized the effect of water vapor on device operation. The role of water as solvent within the thin-film devices was found to increase the current and the initial light output, but at the expense of more rapid decay in light generation.

Introduction

Light-emitting electrochemical cells (LECs) based on $Ru(bpy)_3^{2+}$ salts have been studied for their low operating voltage, high efficiency, high luminance, and simple fabrication methods.[1−5] In these LECs a transition-metal complex and a mobile ion help establish the electric fields at the electrode interfaces that promote charge-transfer reactions at the electrodes.[6] Since the thin film between the electrodes of an LEC functions as an electrolyte, the luminescent characteristics of the device (e.g., response time, operating life) depend strongly on the nature of this material and changes in composition during operation.

However, these LECs exhibit rather short operating lifetimes, which has been ascribed to the generation of a quencher during operation.[4,5] The operating behavior depends on the device's environment in addition to its composition. The turn-on time, to reach maximum luminance after application of the bias voltage, is longer for devices fabricated and operated in a dry nitrogen atmosphere than for those in the ambient atmosphere.[6,7] A suggested quencher arising from water absorption by the film was correlated with decreased device efficiency.[7]

While exploring the effect of residual solvent or absorbed water on ion mobility in these devices, films of a hydrophobic derivative of tris(bipyridine)ruthenium(II) were fabricated using as the counteranion hydrophobic tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, resulting in a much higher turn-on voltage and much lower quantum efficiency. This was attributed to the larger size and much lower mobility of the anion. Solid-state devices constructed from films of $[Ru(bpy)_2(4,4'\text{-}(CH_3(CH_2)_{11}OOC)_2bpy)](ClO_4)_2$, which is completely insoluble in water, showed both a lower current and quantum efficiency than those of an underivatized ruthenium trisbipyridine device. The larger separation between ruthenium centers, resulting in more difficult charge hopping, was hypothesized as the source of these results. These latter approaches, while limiting the amount of adsorbed water due to the film's hydrophobicity, change the nature of the luminescent complex thin film, and hence its underlying electroluminescent behavior.

To study the effect of environment in general and water vapor in particular on the performance of these tris(bipyridine)ruthenium (II)-based LECs, without changing the nature of the film, we performed experiments in which a single film with multiple cathodic contacts was subjected to different atmospheres. A chamber that allowed the exchange of and exposure of a single thin film to different gaseous environments was designed and fabricated. For each experiment, each single film was tested in the absence and then presence of oxygen and then water vapor, or under increasing humidity conditions. The current and electroluminescence transients at a constant applied bias were compared, as well as post-mortem optical images of the contact spots.

Experimental Section

Tris(2,2′-bipyridine)ruthenium(II) perchlorate $[Ru(bpy)_3(ClO_4)_2]$ was used in all studies. It was synthesized by metathesis between $Ru(bpy)_3Cl_2\cdot 6H_2O$ (Aldrich, Milwaukee, WI) and excess sodium perchlorate (Fluka, Milwaukee, WI).[8] The dried product was

---

* Corresponding author. E-mail: ajbard@mail.utexas.edu.

[†] Current address: Sandia National Laboratories, Albuquerque, NM 87185-0613.

(1) Handy, E. S.; Pal, A. J.; Rubner, M. F. *J. Am. Chem. Soc.* **1999**, *121*, 3525−3528.
(2) Gao, F. G.; Bard, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 7426−7427.
(3) Rudmann, H.; Shimada, S.; Rubner, M. F. *J. Am. Chem. Soc.* **2002**, *124*, 4918−4921.
(4) Gao, F. G.; Bard, A. J. *Chem. Mater.* **2002**, *14*, 3465−3470.
(5) Slinker, J.; Bernards, D.; Houston, P. L.; Abruña, H. D.; Bernhard, S.; Malliaras, G. G. *Chem. Commun.* **2003**, 2392−2399.
(6) Buda, M.; Kalyuzhny, G.; Bard, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 6090−6098.
(7) Kalyuzhny, G.; Buda, M.; McNeill, J.; Barbara, P.; Bard, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 6272−6283.
(8) McCord, P.; Bard, A. J. *J. Electroanal. Chem.* **1991**, *318*, 91−99.

10.1021/cm050376h CCC: $30.25

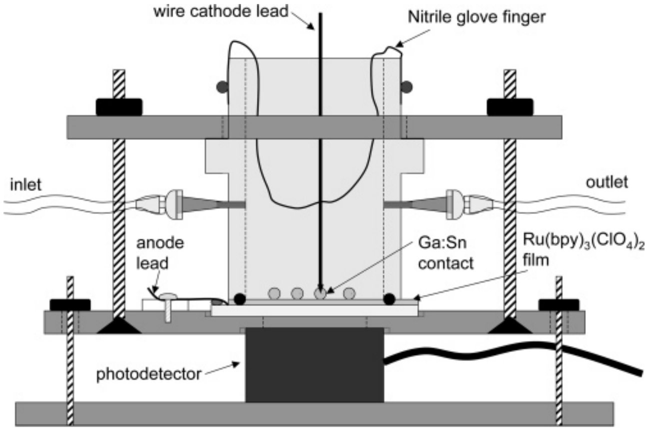

Figure 1. Schematic diagram showing parts of the mini-glove-finger chamber that allows the introduction of different gases, in addition to electrochemical control and measurement coupled with light detection during device operation.

recrystallized using hot acetonitrile (MeCN) and benzene followed by cooling. This precipitate was filtered on a coarse-fritted funnel, washed with methanol, dried with diethyl ether, and then dried further in a vacuum oven at 100 °C overnight. A 4% (wt/vol) solution was made by dissolving $Ru(bpy)_3(ClO_4)_2$ in anhydrous MeCN (Sigma-Aldrich, St. Louis, MO). This solution was filtered using a 0.2 μm pore Teflon syringe filter.

Indium tin oxide (ITO)-coated glass slides, optically transparent electrodes, were used as substrates and served as the anode in all measurements. ITO slides, $\sim$20 Ω/□ (Delta Technologies, Stillwater, MN), were cleaned in a 20% (by volume) ethanolamine (Aldrich) in water mixture, rinsed in sonicated deionized water (Millipore, Billerica, MA), and rinsed further with copious amounts of water, followed by drying in a stream of Ar (Praxair, Danbury, CT). Drops of the liquid metal gallium−tin eutectic (92:8 wt %) alloy, Ga:Sn (Alfa Aesar, Ward Hill, MA), on the $Ru(bpy)_3(ClO_4)_2$ thin film (contact area $\sim$0.2 mm^2) served as convenient cathode contacts, to which connection was made with a metal wire. (A syringe in situ contact, as reported in previous experiments, could not be used, because the high humidity conditions in these experiments produced adsorbed water on the film surface and this caused the syringe reservoir to empty on contact with the surface, with the liquid metal spreading across the film.)

To carry out several measurements on the same film while controlling the environment to which it is exposed, a chamber was designed for the movement of the cathode contact wire and for the introduction and displacement of the various gases. Figure 1 shows a schematic diagram of the chamber. Recessed areas above (square) and below (circle) the hole in the sample chamber base plate (made of aluminum) fit the ITO slide (1 in.^{2}) and the face of the photodetector, respectively. The circular hole in the chamber base plate permitted light to be detected by a photodetector or the film to be imaged from below. A hollow, cylindrical piece of acrylic, machined with a groove for an O-ring at its bottom edge and a rim along its shank, formed the side of the chamber.

A compression seal between the acrylic side and the sample film was made by fastening another plate, having a hole in its center that clears the cylinder top but presses down on the rim, with two nuts tightened on screws attached to the chamber base plate. The inlet and outlet ports each consist of a Luer-lock syringe needle (with its end polished blunt) epoxied in a hole drilled in the side of the chamber. A cut off finger from a Nitrile glove (Fisher, Pittsburgh, PA) fitted over the top opening of the cylindrical chamber and allowed the horizontal and vertical movement of the wire used as the cathode lead. A slightly stretched rubber O-ring sealed the Nitrile membrane along the acrylic cylinder circumference. Four bolts and nuts fixed the chamber plate over the photodetector and to the setup base. The wire was insulated and fastened to an arm attached to a translation stage oriented vertically. The translation stage was mounted on a plate that slid horizontally, but once the wire was positioned above the Ga:Sn drop, the mounting plate could be temporarily secured in place with a bar and fastening screws.

Tygon tubing sections connected by plastic three-way valves were configured to permit the controlled introduction of the desired gas or water vapor into the chamber enclosing the thin film and cathode contacts. A dark fabric—black fake suede (moleskin)—and aluminum foil covered the setup to block ambient light during the measurement.

Light output was measured using a photodetector, model 818-UV with attenuator removed (Newport, Irvine, CA), and optical power meter, model 1830-C (Newport). Electrochemical control and measurement were performed with an Autolab PGSTAT100 (Eco Chemie, Utrecht, The Netherlands) potentiostat/galvanostat that also collected the light power data via its ADC auxiliary input.

To prevent the (uncontrolled) absorption of water, these devices were prepared and enclosed in the specially designed chamber inside a nitrogen-atmosphere drybox (MBraun, Stratham, NH). Solid-state thin films ($\sim$100 nm) of $Ru(bpy)_3(ClO_4)_2$ were made in the drybox by spin-coating (Specialty Coating Systems, Indianapolis, IN) from the 4% (w/v) MeCN solution onto the ITO slide at 2000 rpm. The thin films were subsequently dried at 120 °C for at least 4 h in a vacuum oven attached to the drybox. After cooling, an array of Ga:Sn drops were "printed" from a syringe onto the film surface, and the chamber was assembled and sealed with a three-way valve and a cap at the ends of the inlet and outlet tubes, respectively. The chamber was removed from the drybox and connected to the gas tubing lines. Before the chamber inlet valve was opened, Ar was used to purge all lines of oxygen and, with the exception of the water-filled vacuum trap, moisture. To improve the electrical contact between the anode lead clamp and the ITO surface, a small piece of indium shot was melted on an ethanol-wiped corner of the prepared ITO slide.

Connections were made, and the cathode wire lead was positioned by eye and advanced by the stage translation to the selected Ga:Sn drop. Good electrical contact was verified by performing a voltage sweep from 0 to 1 V, below the onset of charge injection, to observe any measurable low currents. The absence of current rise with increasing voltage bias meant the wire was not in contact and thus the wire was advanced further. High currents ($>\mu$A) indicated a short through the film and thus that contact drop was not used.

To test the various environments, first, Ar (Praxair) was flowed through to test the LEC under inert, dry conditions. Next, O_2 (Praxair) was added to investigate it as a possible quencher. Water vapor entrained in flowing Ar (by bubbling through Millipore water) was introduced to simulate exposure to a humid environment. Last, Ar was flowed through the chamber to purge the headspace of water vapor and dry any water on the surface of the film. A Humitter 50 humidity sensor (TetraTec Instruments, Steinenbronn, Germany) connected to an electrometer (model 6517, Keithley Instruments, Cleveland, OH) capable of providing a digital readout was downstream of the two mixed streams and prior to the stream entering the chamber. In a separate experiment (with a new film), two streams, one of dry Ar and the other of Ar bubbled through water, were proportioned to provide different humidity levels between very low and midrange. Each time the environment was changed the system was allowed to equilibrate for a minimum of 10 min.

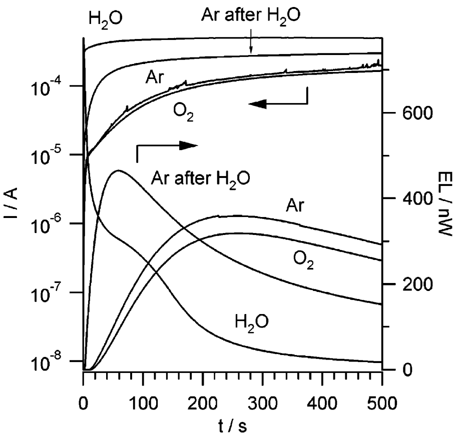

Figure 2. Summary of experimental results [current and electroluminescence vs time] for + ITO|Ru(bpy)$_3$(ClO$_4$)$_2$ film|Ga:Sn(~0.2 mm^2) −, subject to a +2.5 V bias, exposed to different environments in the sequence (each a new contact): Ar, Ar + O_2, Ar + H_2O, Ar (after H_2O).

All data presented were obtained by applying a +2.5 V bias to the LEC device for 1800 s after a 2 s, 0 V conditioning bias was applied. This conditioning bias served two purposes: first, to remove built-in charge established in the film arising from the closed circuit upon making and testing the contact with each liquid metal drop, and second, to establish initial current and light power levels. The short duration of the conditioning bias was probably not sufficient to remove all charge built up in the closed circuit. External quantum and power efficiencies were calculated from the measured current and light power data, assuming that all energy was centered at the emission peak maximum of 660 nm,[2,4] light was reflected back from the liquid metal surface, and only a cone of this light was collected by the photodetector. Furthermore, efficiency calculations incorporated adjustments necessary to account for each drop having a different geometric relationship with the photodetector semiconductor, since only one drop could occupy the center position. All reported current and light data and calculated efficiencies are for the first run at a given contact.

Ga:Sn contacts were imaged through the hole in the chamber base when separated from the photodetector/setup base and placed upon an inverted microscope (Nikon TE 300, Melville, NY). Optical microscope images were obtained using a color CCD camera (MagnaFire-Model599806, Olympus, Melville, NY).

Results and Discussion

Various Environmental Conditions. The possible effects of oxygen and water—in comparison to a dry, inert condition—on the operational stability of a Ru(bpy)$_3$(ClO$_4$)$_2$ thin film LEC device were tested. A compilation of results from a single Ru(bpy)$_3$(ClO$_4$)$_2$ film is given in Figure 2. Both current and electroluminescence are plotted versus time for a +2.5 V applied bias for four conditions tested in the following order: Ar, O_2, H_2O, and Ar after being purged for 12 h. At all times Ar was flowing; i.e., O_2 and H_2O (water vapor) were additions, since pure O_2 oxidized the liquid metal cathode, resulting in an unstable contact, and water alone would dissolve the film as well as itself be a liquid electrolyte. The O_2 and water vapor each were added using a Y-connector to mix this stream with the dry Ar stream in a ratio from approximately 25:75 to 50:50. Each curve represents a different cathode contact with an area of ~0.2 mm^2.

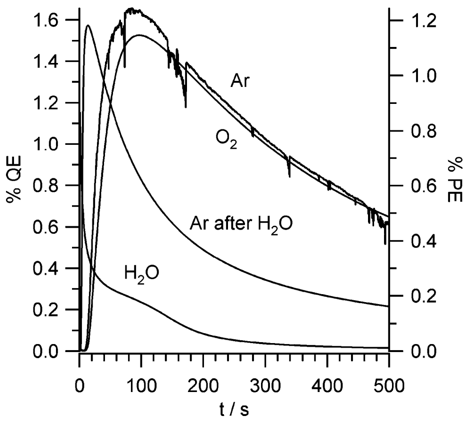

Figure 3. Summary of calculated quantum and power efficiencies for the data in Figure 2. For a constant applied voltage, the power efficiency is a constant multiple of the quantum efficiency, which is 0.75 in this case.

The current transients exhibited an initial increase in magnitude followed by a leveling off. Those for the Ar and O_2 conditions were similar and approximately an order of magnitude lower than the current transient for the film in the presence of water vapor. Also, the level current regime was attained more quickly in the presence of water vapor. The film previously exposed to water vapor, but tested in a dry, inert atmosphere, yielded a current transient between those for the dry and humid conditions. Similarly, the electroluminescence transients showed three types of responses according to the atmospheric conditions: dry, humid, or dry after previous humidity exposure. For the dry conditions (with either Ar or O_2), the onset of light output was delayed and its increase more gradual. In contrast, the generation of light was observed immediately upon voltage application for the film in the presence of, or with prior exposure to, water vapor. With added humidity, an immediate, large burst of light was generated, followed by a sharp decay in output. With removal of water vapor from the atmosphere, the device generated more light at shorter times than the dry films, but did not sustain this level, generating less light at longer times (>200 s).

The calculated quantum and power efficiencies for these experimental results are plotted versus time in Figure 3. These data, which are proportional to the ratio of light output to current input, exhibit the same trends as exhibited by the electroluminescence transients. For a constant applied voltage, the difference between the quantum and power efficiencies is a constant factor that depends on the photon energy and the applied voltage. For the quantum efficiency, the ratio of light power ($W = J\ s^{-1}$) to current ($C\ s^{-1}$) is divided by the ratio of energy, in eV, of the emission ($1240/\lambda$,[9] where λ is the wavelength in nm) to the charge of an electron. The power efficiency is obtained by simply dividing the ratio of light power to current multiplied by the applied voltage. Thus, for a peak emission of 660 nm,[2,4] which was assumed to be the wavelength of all collected light, and for an applied bias of +2.5 V, the factor to convert quantum efficiency to power efficiency is 0.75. The adjustments incorporated in the calculations to account for the Ga:Sn drops being off-center from the photodetector axis amounted to a small correction, typically less than 6%.

Interestingly, the peak efficiencies all lie in a range of less than one percentage point. This observation points to the electroluminescent emission scaling with the current, independent of the operating environment. However, the time scales for the processes to reach a maximum evidently depend on the environment.

The electroluminescence transients in Figure 2 demonstrate the poor stability of these devices with respect to long-term light production, especially in the presence of water vapor. Exposure or even previous exposure to water vapor seriously degraded the magnitude of light for a given applied voltage. However, the response time to the application of the voltage was enhanced by exposure to humidity.

Together, these results suggest that the $Ru(bpy)_3(ClO_4)_2$ film absorbs water from its environment. The mechanism for these devices has previously been demonstrated to be electrochemical in nature.[6,10] The water absorbed by the film can serve as a solvent, thus enhancing the anion mobility, as well as play the role of ligand and exchange for bpy in the excited state.

The trend to shorter onset times for light generation from films exposed to water vapor agrees with the observation that the light from LECs made and tested in the ambient environment turn on sooner than those made and tested inside a drybox.[7] The effect of water substituted for bpy on the excited complex in solid-state thin films was illustrated in the response of a series of films made from various mixtures of the unadulterated $Ru(bpy)_3^{2+}$ complex and the diaquo complex $Ru(bpy)_2(H_2O)_2^{2+}$.[7] Only a small amount ($<4\%$) of the hypothesized quencher, $Ru(bpy)_2(H_2O)_2^{2+}$, was sufficient to diminish the peak efficiency of the device. Correspondingly, water molecules from the humid environment above the film absorbed by the film can exchange with the bpy to produce this diaquo complex.

Various Humidity Levels. In a separate set of measurements for a different film, the humidity levels were varied to investigate more fully the effect of water on LEC operational stability. Figure 4 shows the current and the electroluminescence transients for a series of humidities exposed to a new film starting with the drybox condition and increasing to high humidity (63% relative humidity). The trends exhibited here lie within those shown previously. With increasing humidity the current increases in magnitude and the current reaches a more steady level sooner. At the highest relative humidity levels tested (47%, 48%, and 63%) a peak in the current was observed in the time frame of the experiment (1800 s). The electroluminescence transients reveal a low and steady level for the dry and low relative humidity levels and, for the high humidities, an immediate high and brief light generation followed by a sharp decrease to a level at or below those of drier conditions. The amount of light collected in these experiments depended not only on the environmental conditions but also on slight variations in the size and location of the contact.

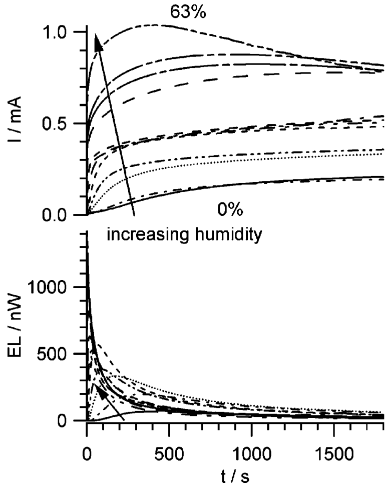

Figure 4. Summary of experimental results [current and electroluminescence vs time] for + ITO|new single $Ru(bpy)_3(ClO_4)_2$ film|Ga:Sn($\sim$0.2 mm^2) −, subject to a +2.5 V bias, exposed to increasing relative humidity (each level a new contact) from drybox condition to H_2O water vapor condition as in Figure 2.

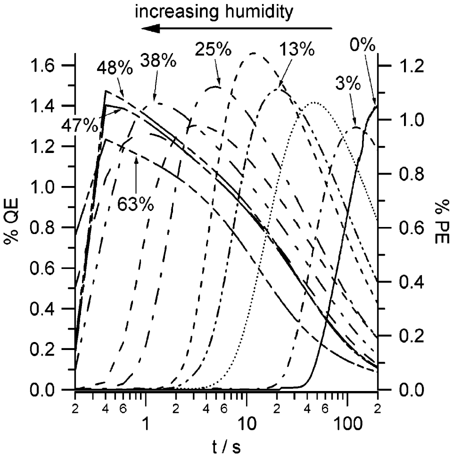

Figure 5. Summary of calculated quantum and power efficiencies for data in Figure 4. For a constant applied voltage, the power efficiency is a constant multiple of the quantum efficiency, which is 0.75 in this case.

The corresponding quantum and power efficiencies were calculated with correction for geometry between the Ga:Sn drop and photodetector and are plotted versus time (logarithmic scale) in Figure 5. The peak quantum efficiencies were scattered between 1.2% and 1.65%, without any apparent trend with relative humidity. The trend of shorter times for turn-on and for reaching peak efficiency with increasing humidity is evident.

The scatter in peak efficiencies probably represents experimental variance arising from using different contact drops located on different portions of the thin film as well as the estimation of geometry between the contact drop and the photodetector face. The level of precision in individual measurements is suggested by a comparison of the efficiency transients for the 47% and 48% relative humidity conditions.

Characteristic times of the electroluminescence and quantum efficiency transients were extracted from the curves and are plotted versus the relative humidity in Figure 6. The trend in shorter times for turning on and reaching maximum electroluminescence and quantum efficiency with higher relative humidity is clear. Similarly, a shortening of the half-life of the light generation, $t_{1/2}$, is observed for more humid

---

(9) Mayer, J. W.; Lau, S. S. *Electronic Materials Science: For Integrated Circuits in Si and GaAs*; Macmillan: New York, 1990; p 30.

(10) Li, Y. F.; Cao, Y.; Gao, J.; Wang, D. L.; Yu, G.; Heeger, A. J. *Synth. Met.* **1999**, *99*, 243−248.

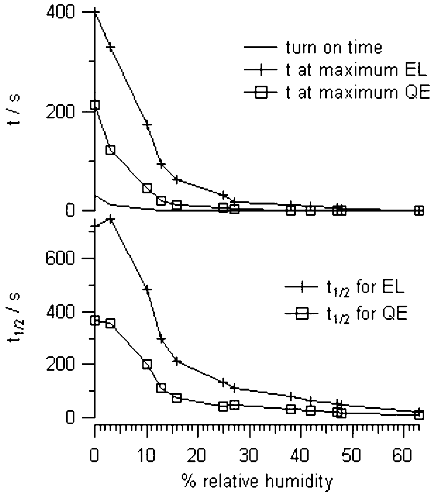

Figure 6. Graphs of characteristic times plotted versus relative humidity.

conditions. Clearly the introduction of water into the film from even a small amount of moisture in the environment results in the degradation of the light-generation mechanism. Each time characteristic decreases gradually with increasing humidity. Above 25% relative humidity, smaller changes in these characteristic times occur.

The first LEC devices reported from our laboratory included an epoxy coating.[2,4] This epoxy effectively encapsulated the film and prevented exposure to moisture in the environment. Those LEC devices were prepared in the laboratory, outside a drybox. Thus, based on the present results, increased lifetimes, as well as turn-on times, would be expected had the devices been prepared and encapsulated inside a drybox.

Optical Images of Contacts. Previous studies of these kinds of LECs showed that bubbles sometimes formed on the contacts, especially in the cells without epoxy coatings. Figure 7 shows selected optical images of contacts for relative humidities spanning the range tested. Figure 7a shows a contact before any humid gas was introduced to the chamber. Parts b through f of Figure 7 each show optical images of the contacts after the completed tests for the relative humidity levels 0%, 25%, 42%, 47%, and 63%. This series of images of the contacts after testing revealed that bubbles formed between the Ga:Sn drop and the film for environments containing water vapor at concentrations greater than ~45% relative humidity. These bubbles most likely arise from the reduction of water at the cathode to form H_2 and increase in size with increasing humidity level and bias voltage duration, although alternative mechanisms for bubble formation are possible. Note the current transients peak for the more humid conditions (see Figure 4). A decreasing electrode area stemming from growing bubbles at the electrode interface can explain the decreasing current with continued operation. Also, the bubbles originate along the periphery of the contact drop, thus suggesting a diffusion mechanism for water absorption and subsequent gas evolution. An analogous growth from the edge of the contact (a defect in the cathode layer or a pinhole) has been observed for dark spot formation in tris(8-hydroxyquinoline)aluminum film devices.[11,12]

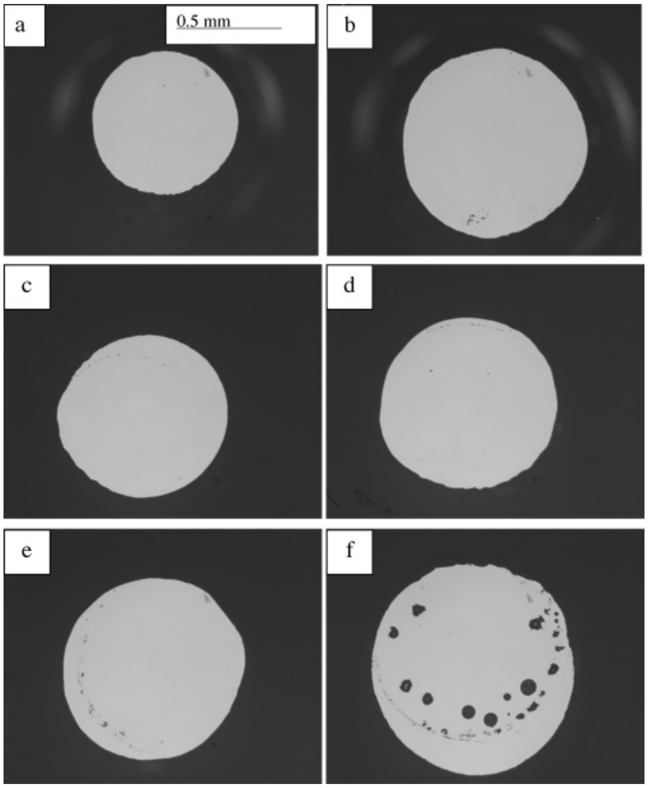

Figure 7. Optical images of Ga:Sn contacts for the $Ru(bpy)_3(ClO_4)_2$ film LEC tested in increasingly humid environments measured in relative humidity (RH): (a) pristine, (b) 0% RH, (c) 25% RH, (d) 42% RH, (e) 47% RH, (f) 63% RH.

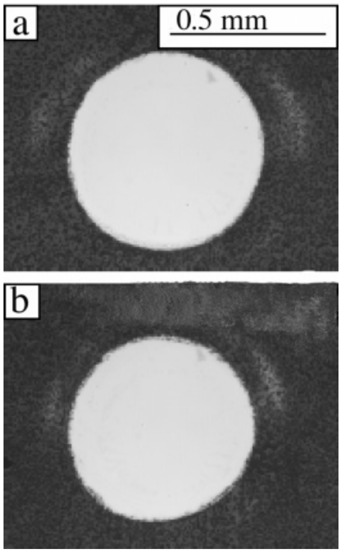

Figure 8. Optical images of Ga:Sn contacts for the $Ru(bpy)_3(ClO_4)_2$ film LEC tested in (a) Ar and O_2 and (b) after 12 h of Ar purging following Ar and H_2O exposure. N.B., since both images were taken after completion of all tests on this film, the film surrounding the contacts looks mottled rather than glassy due to its exposure to high humidity during part of the tests.

Optical images of contacts for the first film tested in various gaseous environments also were obtained. Figure 8 shows the contacts for (a) the Ar and O_2 condition and (b) the dried-by-Ar-purging condition after the film had been exposed to high relative humidity. These images reveal that

---

(11) Lim, S. F.; Wang, W.; Chua, S. J. *Adv. Funct. Mater.* **2002**, *12*, 513−518.

(12) Schaer, M.; Nuesch, F.; Berner, D.; Leo, W.; Zuppiroli, L. *Adv. Funct. Mater.* **2001**, *11*, 116−121.

bubbles were not formed during their tests. Thus, the active presence of water vapor is necessary for the formation of bubbles at the Ga:Sn contact. Furthermore, the absence of bubble formation with these two conditions indicates that absorbed water is the source of performance degradation and not simply the additional Faradaic reaction of water electrolysis. Note that the morphology of the surrounding film has changed due to absorbed water after humidity exposure and prior to imaging. Crystal formation and growth in tris-(8-hydroxyquinoline)aluminum films have been reported to result from exposure to humidity.[13] Although this report claims that device failure stems from cathode delamination induced by the crystalline clusters, the nature of the liquid metal contact in the present work excludes this possibility.

A further possible step in this investigation would be to study the effect of combined moisture and oxygen on the degradation of these LEC devices. An investigation of the effects of atmospheric exposure on tris(8-hydroxyquinoline)-aluminum, AlQ_3, films found that both water and oxygen degraded the photoluminescence over time.[14]

Conclusions

These studies of the effect of gaseous environment reinforce earlier work and suggest that moisture in the film is an important factor in film conductivity and LEC lifetime. Faster turn-on is seen in the presence of moisture, but the lifetime is seriously degraded. The device should be encapsulated at least for the purpose of preventing performance degradation from absorbed moisture. The importance of solvent in device operation and stability has also been demonstrated in experiments involving operating the LECs in high vacuum environments.[15]

Acknowledgment. We acknowledge support of this research from the National Science Foundation (CHE 0202136) and the Robert A. Welch Foundation through the Center for Nano- and Molecular-Science and Technology.

CM050376H

---

(13) Aziz, H.; Popovic, Z.; Xie, S.; Hor, A.-M.; Hu, N.-X.; Tripp, C.; Xu, G. *Appl. Phys. Lett.* **1998**, *72*, 756−758.

(14) Djurisic, A. B.; Lau, T. W.; Lam, L. S. M.; Chan, W. K. *Appl. Phys. A-Mater. Sci. Process.* **2004**, *78*, 375−380.

(15) Zhao, W.; Liu, C.-Y.; Wang, Q.; White, J. M.; Bard, A. J. *Chem. Mater.* Submitted.