

Effect of Residual Solvent on Ru(bpy)₃(ClO₄)₂-Based Light-Emitting Electrochemical Cells

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The effect of residual water (H₂O) and acetonitrile (MeCN) on the performance of tris(2,2'-bipyridine)-ruthenium(II) perchlorate (Ru(bpy)₃(ClO₄)₂)-based light-emitting electrochemical cells (LECs) was investigated by treating and operating the cells under high-vacuum conditions. The results show that treating the Ru(bpy)₃(ClO₄)₂ film in a conventional vacuum oven (50–100 mTorr) at 125 °C for 48 h is not enough to dry the films. Simply leaving the film in a high vacuum (2×10^{-7} Torr) for 12 h raised the turn-on voltage to 2.6 V from 2.1 V and improved the device stability. After further drying of the film in an ultrahigh vacuum (UHV) chamber (6×10^{-10} Torr) at 143 °C for 4 h, the film still released H₂O and MeCN. When the film was baked in UHV for 24 h, the turn-on voltage rose to 6.1 V and the device was further stabilized. As indicated earlier, solvent increases the mobility of the anions and, thus, facilitates the formation of a double layer at the electrode interfaces. When the film was dried in UHV, the film resistance increased, resulting in a higher turn-on voltage with weaker emission. However, H₂O also probably leads to quencher formation, so its removal increases stability.

Solid-state, thin film, electroluminescent (EL) devices based on tris(2,2'-bipyridine)ruthenium(II) (Ru(bpy)₃²⁺) complexes have been of interest because they are easy to fabricate and show good emission properties at low voltages.^{1–24} These have been shown to be light-emitting electrochemical cells

(LECs), generally, in which the migration of the mobile anions under the external applied voltage causes the formation of an electrical double layer at the interface between the electrode and the EL layer, therefore facilitating interfacial charge injection. This results in an operating voltage near the optical band gap of the EL molecules and strong electroluminescence.^{5,6,25} In previous studies of these LECs,^{4–24} the films, after spin coating from MeCN solutions, were usually dried in a conventional vacuum oven (evacuated with a mechanical pump) at the temperature of 125 °C, and the films were assumed to be “dry”. An important question is the role of traces of solvents in the operation of the cell and especially in the anion mobility. In previous publications,^{11,15} the response time (which is defined as the time to reach maximum EL intensity at a certain voltage) was shown to be considerably shorter when the device was tested under ambient conditions rather than within a drybox. Devices that were both fabricated and tested in a drybox showed less intense luminescence, but more stable operation, which suggested that the Ru(bpy)₃²⁺ devices are very sensitive to the ambient environment. Residual solvents also affect the lifetime of the device under operating conditions and the formation of a quencher, such as Ru(bpy)₂(H₂O)₂, by reaction of the excited state, Ru(bpy)₃^{2+*}, with residual H₂O proposed as the cause of the instability.¹⁵

In this work, we studied these cells under a high vacuum (2×10^{-7} Torr) and an UHV (6×10^{-10} Torr) and have

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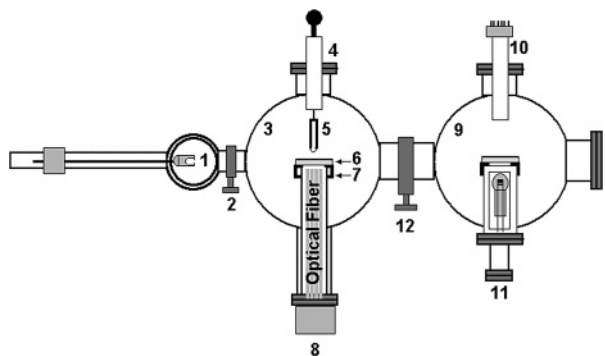


Figure 1. A schematic view of the UHV system for $\text{Ru}(\text{bpy})_3^{2+}$ film treatment and device characterization. 1, Sample loading chamber (2×10^{-6} Torr); 2, gate valve; 3, current–light emission–voltage test chamber (2×10^{-7} Torr); 4, tip motion microstage; 5, Ga–In tip; 6, $\text{Ru}(\text{bpy})_3^{2+}$ film/ITO-glass; 7, sample puck; 8, optical power meter; 9, UHV chamber (6×10^{-10} Torr); 10, mass spectrometer; 11, sample annealing stage; and 12, gate valve.

shown that the film, dried in a conventional vacuum oven (50–100 mTorr and 125 °C) for 48 h, still contains H_2O and MeCN (the organic solvent used to prepare all $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ films in this work). The devices displayed different operational behavior under these conditions, including a higher operating voltage, slower response time, and better stability.

Thin films of $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ were spin-coated on indium tin oxide (ITO) coated glass ($20 \text{ } \Omega/\text{cm}^2$, Delta Technologies) as described previously.^{26,27} The films were dried in a conventional vacuum oven (50–100 mTorr) at 125 °C for 48 h. Ga–In eutectic (75.5:24.5 wt %, mp 15.7 °C, Alfa-Aesar) was dropped into a thin tube of spiraled copper wire (item 5 in Figure 1) (inner diameter: 0.5 mm) and brought into contact with the film by a microstage (item 4 in Figure 1). The electrode contact area was about 1 mm in diameter. Three kinds of $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ devices were fabricated and tested in this work: (1) Following spin coating, the film was dried in a conventional vacuum oven (50–100 mTorr) at 125 °C for 48 h, the device was tested in air (designated LEC-1). (2) The film from (1) was left in a high-vacuum chamber (2×10^{-7} Torr) for 12 h and tested in the high-vacuum chamber (designated LEC-2). (3) The film from (2) was annealed at 143 °C in the UHV chamber (6×10^{-10} Torr) for 24 h and tested in the high-vacuum chamber (2×10^{-7} Torr) (designated LEC-3).

As shown in Figure 1, the vacuum system for the experiment includes three consecutive chambers, isolated by two gate valves (2 and 12), for sample loading (1), testing (3), and thermal treatment (9). Both sample loading and testing chambers are evacuated by turbo pumps with base pressures of 2×10^{-6} and 2×10^{-7} Torr, respectively. The thermal annealing chamber is evacuated by a liquid N_2 trap cooled diffusion pump with a typical base pressure of 6×10^{-10} Torr. The testing chamber is armed with a bundle of glass optical fibers ($\phi \sim 3 \text{ mm}$ for each). One end of the bundle is located underneath the sample and the other closely attaches to the inner surface of the viewport. The optical

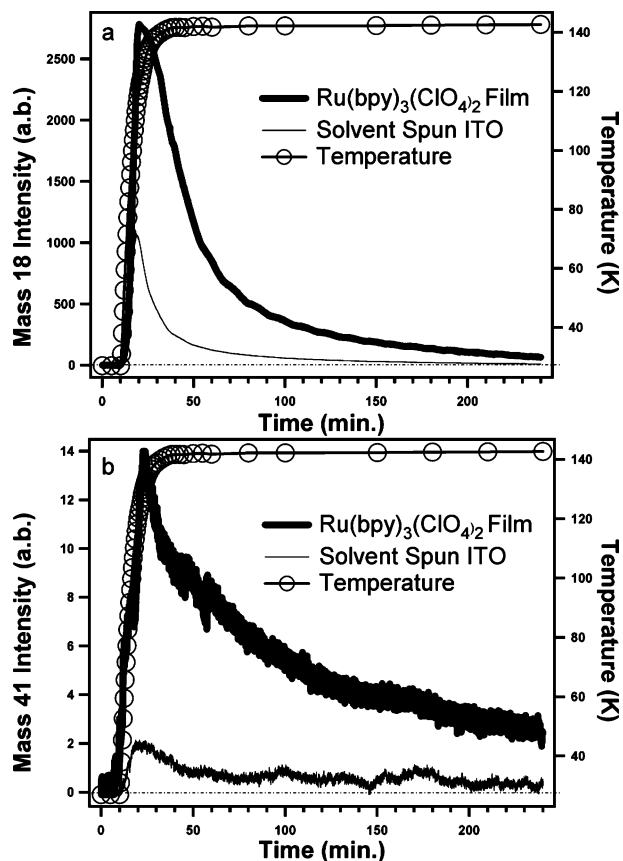


Figure 2. (a) Water and (b) MeCN desorption vs time from $\text{Ru}(\text{bpy})_3^{2+}$ film annealed at 143 °C in a UHV chamber (thick solid lines). The acetonitrile-spun ITO is the reference (thin solid lines). The temperature of the sample puck was also recorded and is given in the figure. The thin dashed lines are a guide for baselines.

power meter (8) is mounted onto the outside of the viewport to measure the EL. The sample annealing stage (11) was made of a 1 in. diameter hollow copper rod (one end closed) with a halogen lamp installed inside to heat the stage. The whole stage is isolated from the chamber by a ceramic support. A K-type thermocouple is attached to the top part of the stage to measure and regulate the temperature [Eurotherm (818PT4)]. The stage top part was polished flat to increase the thermal conductivity between the stage and the sample puck, which is also made of copper. The sample (6) is fixed on the top of the puck (7) by two screws. The annealing stage was usually heated to 200 °C for 24 h and then cooled to 150 °C for sample treatment; thus, the background contamination is minimized. When the sample puck is loaded onto the heating stage, the heating stage and the sample puck eventually reach the temperature equilibrium at 143 °C. A mass spectrometer (10 in Figure 1) (UTI Instruments, Model 100C) is situated in front of the sample at a distance of 4 in. In this experiment, a spin-coated film was baked in a conventional vacuum oven and then loaded into the vacuum system. The sample was left in the test chamber for 12 h and then transferred to the annealing chamber for treatment.

The mass spectrometer tracked the concentration change of H_2O (mass 18) (Figure 2a) and MeCN (mass 41) (Figure 2b) in the UHV chamber. Before the sample puck was loaded onto the annealing stage, the mass spectrometer measured H_2O and MeCN for 10 min as the baseline. Then, the sample

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puck was moved onto the annealing stage, and the temperature of the sample puck (measured from an identical calibration sample puck) quickly rose and eventually stabilized at 143 °C over a period of 25–30 min. Both H₂O and MeCN showed a sharp rising for the first 10 min and an exponential decaying afterward. Note that a reference experiment was also carried out in which a sample puck with the ITO substrate, where acetonitrile was spun onto and baked in the conventional vacuum oven as the Ru(bpy)₃(ClO₄)₂ film, was annealed in the same way with both masses 18 and 41 being recorded. The data presented in Figure 2 show both cases in comparison. The difference of the corresponding curves represents the pure effect of Ru(bpy)₃(ClO₄)₂ complex. Even after 4 h annealing at 143 °C under UHV conditions, the Ru(bpy)₃²⁺ film still slowly desorbed both H₂O and MeCN (thick solid line in Figure 2), but the desorption of the residual solvents reached the baseline (dashed lines in Figure 2) for the bare ITO substrate with acetonitrile spin-coated (thin solid lines in Figure 2). The chamber base pressure was about 2×10^{-9} Torr, which is higher than the chamber pressure before the sample puck was loaded onto the annealing stage (6×10^{-10} Torr). The sample was kept under the annealing conditions for another 20 h, without the mass spectrometer tracking desorption. After this time, a total of 24 h annealing, the chamber pressure had dropped to 6.5×10^{-10} Torr, which was very near the starting base pressure, indicating that the desorption had essentially ceased. In discussing the desorption intensities of H₂O and MeCN, the sensitivity factor of MeCN is unknown in mass spectrometry and H₂O has a sensitivity factor 1.17, so we assume that MeCN has a similar sensitivity factor as H₂O (as a similar example, CH₄ has a sensitivity factor of 1.08). Figure 2 shows that the intensity of the H₂O desorption peak is 192 times that of MeCN, suggesting that the residual H₂O is the main component and MeCN a minor component in the film; it is difficult to know the absolute amounts of H₂O and MeCN desorbed without a multistep calibration. The results indicate that it is very difficult to remove the last traces of solvents (H₂O and MeCN) from the film. Both H₂O and MeCN are polar (dielectric constants, 79 and 37, and dipole moments, 1.0 and 0.46, respectively), so they can interact strongly with the ions in the film, Ru(bpy)₃²⁺ and ClO₄⁻, making it very difficult to remove from the film.

The effect of residual solvent on the device performance is shown in Figure 3. LEC-1 had a turn-on voltage of 2.1 ± 0.2 V, comparable with previous reports.⁶ However, the turn-on voltage of the LEC-2 and LEC-3 increased to 2.6 ± 0.2 V and to 6.1 ± 0.2 V, respectively. This observation indicates a much higher resistance in the dried films due to the lower mobility of ClO₄⁻ without solvent. The Ru(bpy)₃²⁺ is assumed to be immobile because of its bulky size.

Obviously, the residual MeCN and H₂O play an important role in LEC operation. This is in agreement with previous observations^{11,15} that devices fabricated and tested in a drybox and in air showed dramatically different operational characteristics.

Figure 4 displays the electroluminescent intensity versus the operating time, *t*, for LEC-1, LEC-2, and LEC-3. The *i*

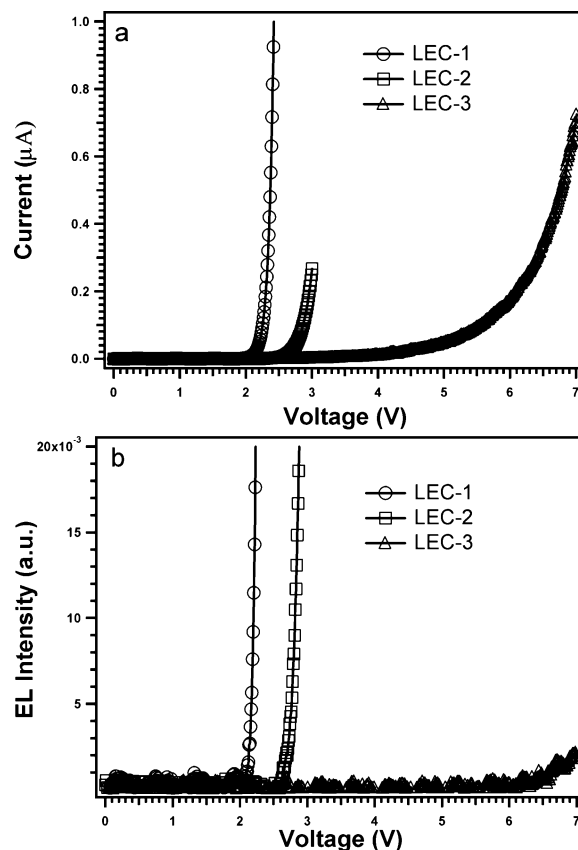


Figure 3. (a) Current and (b) EL intensity vs voltage for glass-ITO/Ru(bpy)₃(ClO₄)₂/Ga-In devices. Here, the Ru(bpy)₃(ClO₄)₂ films were treated under three kinds of experimental conditions: the regular vacuum oven (LEC-1), a high-vacuum chamber (LEC-2), and annealed in UHV (LEC-3).

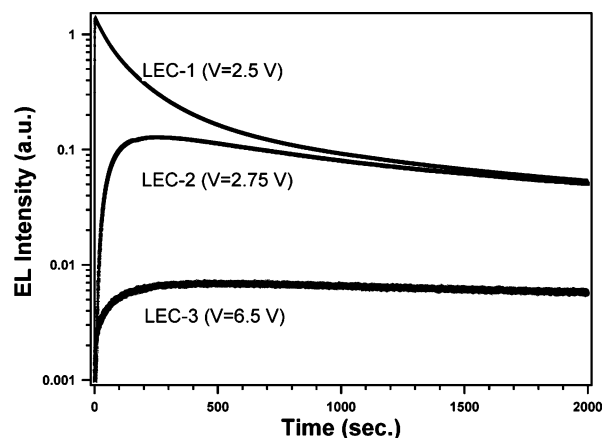


Figure 4. EL intensity vs time for glass-ITO/Ru(bpy)₃(ClO₄)₂/Ga-In devices. Here, the Ru(bpy)₃(ClO₄)₂ films were treated in three kinds of experimental conditions: the regular vacuum oven (LEC-1 at 2.5 V), a high-vacuum chamber (LEC-2 at 2.75 V), and annealed in UHV (LEC-3 at 6.5 V).

vs *t* shows a similar trace, but is not presented here. Even with a much lower operating voltage (2.5 V), LEC-1 shows strong light emission along with a fast response (2.5 s), but the EL intensity, *I*, decayed by 96% in 2000 s. LEC-2 was operated at a little higher voltage (2.75 V) with the maximum light intensity being about one-tenth that of LEC-1. The response time was much longer, 200 s, but *I* decayed by only about 60% after 2000 s. For LEC-3, at the voltage of 6.5 V, the maximum EL intensity is about one-tenth that of

LEC-2 and one-hundredth of LEC-1. The response time was further delayed (400 s); however, the light intensity only decayed by about 9% in 2000 s operation. These results again demonstrated the importance of solvent in the mobility of the ions. The apparent stabilization is not so straightforward, however, because previous studies with “wet” cells have shown that operating them at lower intensities prolonged their life. This is consistent with the formation of quencher from the excited state, being the major route of decay of emission. Since the driest film operates at one-hundredth the intensity, a significantly better lifetime is expected. Previous studies^{11,15} have proposed that the primary reason for the irreversible $\text{Ru}(\text{bpy})_3^{2+}$ LEC degradation is the generation of a quencher in a thin layer near the cathode (where the EL is observed) from a side reaction of $\text{Ru}(\text{bpy})_3^{2+*}$, probably $\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2^{2+}$. This experiment proves that a significant amount of H_2O exists within the film after it is baked in a regular vacuum oven, which further supports the previous assumption. The role of MeCN and the mechanism of decay in the film are less clear. Interestingly, hysteresis was still seen in dried film, at a given voltage (6.5 V) (LEC-3 in Figure 4); the light emission takes 200–300 s to rise to the maximum,

indicating lower carrier mobility and the possible presence of the charge traps within the films.

We conclude that the operating characteristics of tris(2,2'-bipyridine)ruthenium(II) complex-based light-emitting devices are strongly influenced by residual solvents (H_2O and MeCN). Films, dried in a vacuum (50–100 mTorr) oven (125 °C) for 48 h, still contain the residual solvents. Pumping film in a high-vacuum chamber (2×10^{-7} Torr, where the water concentration is approximately 1 order of magnitude less than a drybox) causes an increase in the turn-on voltage (to 2.6 V from 2.1 V) and shows less intense light emission. Even in treating in a UHV environment (6×10^{-10} Torr) and 143 °C, it takes more than 4 h to drive H_2O and MeCN from the film. This device shows a turn-on voltage of 6.1 V, with much lower light emission intensity.

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