Lifetime study of polymer light-emitting electrochemical cells

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The lifetime and degradation characteristics of frozen-junction polymer light-emitting electrochemical cells have been studied. Two seemingly minor factors, the end group of the same luminescent polymer and the type of substrate on which the device is constructed, have shown profound effects on the stress behaviors of these devices operated at a nominal operating temperature of 200 K. In devices made on glass substrates, an anomalous large increase in light intensity and driving voltage has been observed under constant current stress measurement. This has been attributed to the relaxation of the electrochemical doping, which leads to reduced photoluminescence quenching and increased resistance in the polymer film. The doping relaxation is accelerated by the poor thermal conductivity of glass substrate, which causes significant temperature rise in the device due to self-heating. Evidence also suggests that doping relaxation can even occur at below the glass transition temperature of the polymer electrolyte. All devices are shown to be short lived when operated at or above 250 K due to fast doping relaxation. However, devices made on sapphire substrates based on 3,5-dimethyl phenyl-terminated poly[5-(2′-ethylhexyloxy)-2-methoxy-1, 4-phenylene vinylene] are remarkably stable when operated at 200 K, with an estimated half-life of 700 h even when stressed at a very high current density of 1 A/cm^2.
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I. INTRODUCTION

Electroluminescence (EL) from luminescent conjugated polymers is commonly achieved in polymer light-emitting diodes (PLEDs).[1–3] Polymer EL can also be realized via the formation of a light-emitting *p-n* junction by *in situ* electrochemical doping in a solid-state device known as a polymer light-emitting electrochemical cell (LEC).[4,5] The operating mechanism of LECs is fundamentally different from that of PLEDs and is best illustrated with the recent demonstration and direct imaging of planar LECs with an extremely large interelectrode spacing (up to 11 mm).[6,7] Such scalability is unimaginable in PLEDs, which are metal/insulator/metal diodes with a highly resistive active layer. Despite possessing some very attractive device characteristics, such as low operating voltage and insensitivity to the choice of electrode materials, LECs are not perceived as suitable candidates for potential display and lighting applications due to their slow response and inferior operating lifetime. The latter is evidenced by the very short LEC lifetimes reported in literature, typically on the order of 100 h or less.[5,8–12] By comparison, half-lives in excess of 10 000 h at display brightness are routinely achieved in PLEDs.[2,13]

The lifetime of a LEC is adversely affected by many factors. LECs are made with the same luminescent conjugated polymers commonly used in PLEDs [e.g., poly[5-(2′-ethylhexyloxy)-2-methoxy-1, 4-phenylene vinylene] MEH-PPV], which are easily degraded by oxidation or photo-oxidation.[14–16] In addition, the salt content in the LEC film makes it hydroscopic and susceptible to moisture. A more serious problem lies with electrochemical doping itself, which can lead to rapid degradation by "overdoping" when the device is operated outside the electrochemical stability window. As a result, thin sandwich LECs are rarely operated above 4 V. This limits the light output attainable from a LEC.

Many LEC drawbacks are caused by the existence of mobile ions which can be overcome by operating the device in a "frozen-junction" mode.[17] This is achieved by cooling a fully turned-on device to below the glass transition temperature (T_g) of the polymer electrolyte used. The ions are immobilized when the chain segmental motion of the ion-solvating polymer ceases at temperatures below T_g. Frozen-junction LECs display submicrosecond response time and a linear relationship between EL intensity and device current. A frozen-junction LEC was stressed under constant current at 200 K, which saw a 5% drop in EL intensity after 14 h.[18] Frozen-junction-like behaviors have also been observed at room temperature in LECs using crown ether as the solid electrolyte, but no lifetime figure was presented.[19]

Despite encouraging initial results, the lifetime and degradation of frozen-junction LECs have never been characterized in detail. Recently we have demonstrated extremely large planar LECs with millimeter interelectrode spacings.[6] Fluorescence imaging of these massive planar devices makes it possible to distinguish individual *p*- or *n*-doping propagation rate as a function of voltage bias and temperature.[20] Moreover, a static doping profile at 200 K is visualized by direct imaging.[21] Planar frozen-junction LECs during constant current stress display an intriguing net luminance increase.[22] Since the EL intensity at the end of testing cycle (~150 h) is higher than the initial value, no half-life was obtained. The unexpected stress behavior was explained in terms of reduced electron mobility, which can lead to increased electron capture radius and therefore EL efficiency.

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Here we present systematic study of frozen-junction LEC degradation as affected by stress current, stress temperature, type of substrate, and luminescent polymer. We show strong evidence that at 200 K the frozen *p*-*n* junction exhibits slow doping relaxation that can dictate the stress behavior of the devices. Doping relaxation leads to reduced PL quenching in the light-emitting junction region and is the most probable cause of the above-mentioned EL increase during constant current stress. Nevertheless, LECs made with certain combination of luminescent polymer and substrate exhibit remarkable stability.

II. EXPERIMENTAL DETAILS

The planar LECs in this study were prepared on polished sapphire squares ($15\times15\times1$ mm^3) or polished Corning 1737F aluminosilicate glass squares ($15\times15\times1.1$ mm^3). The substrates were cleaned by ultrasonication in acetone and isopropanol, followed by UV-ozone treatment for 10 min. The luminescent polymer used is poly[5-(2′-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV), terminated by either 3,5-dimethyl phenyl or polysilsesquioxane. The polymer electrolyte consists of an ion-solvating polymer, poly(ethylene oxide) (PEO) (M_n=2*M*), and lithium trifluoromethanesulfonate (Li triflate).

A luminescent polymer and polymer electrolyte were dissolved in their common solvent, cyclohexanone, to create master solutions of concentrations of 1.5% (w/v) (i.e., 15 mg/ml) and 2% (w/v), respectively. Suitable amounts of the two solutions were then mixed together to create a LEC solution containing MEH-PPV, PEO, and Li triflate in a weight ratio of 15:20:4. The LEC solution was spin cast onto the substrate at 1400 rpm to form a polymer film of about 0.65 μm in thickness. After drying at 50 °C for at least 3 h, 100 nm thick aluminum electrodes were evaporated on top of the polymer film through a shadow mask to complete the device. The spacing between the aluminum electrodes is 0.6 mm. The length of the electrodes is 8 mm. All devices were fabricated in a custom MBraun double glovebox/evaporator system filled with dry nitrogen. Both the oxygen and moisture levels in the glove boxes were below 1 ppm.

The devices were tested in an optical cryostat under 18 mtorr vacuum. A Keithley 237 source measurement unit, a Keithley 2010 multimeter, and a Hamamatsu amplified photodiode were used to drive the devices and to measure the current–voltage–light intensity characteristics of the devices.

III. RESULTS

All devices employed in this work are planar LECs with an interelectrode spacing of 0.6 mm, same as those used in our preliminary study.[22] The submillimeter gap is small enough to allow significant current flow and EL output at frozen-junction temperatures while large enough to ensure that the EL emission zone is far from both contacts to avoid any possible electrode quenching of luminescence. The device characteristics of these planar LECs are truly bulk limited. They offer the unique opportunity to study the "intrinsic" degradation mechanisms associated with the polymer itself. In fact, no "black spots" or any electrode related degradation has been observed in our devices during stress. All frozen-junction devices consistently exhibit very low EL turn on voltage (~5 V) and extremely smooth and highly reproducible current-voltage (*I*-*V*) characteristics.

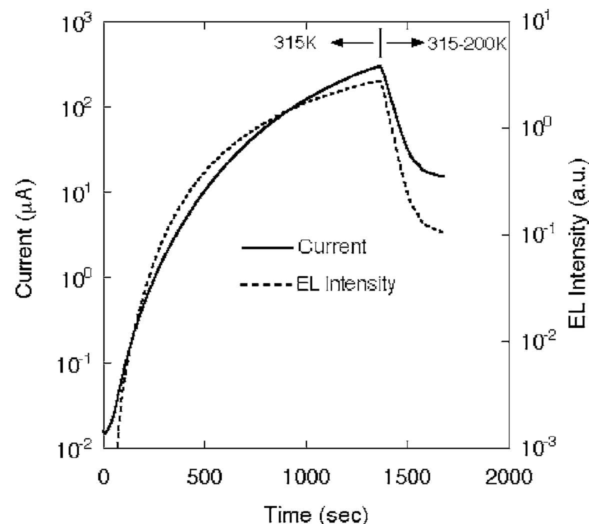

FIG. 1. Turn on and cooling characteristics of a 0.6 mm planar LEC. The device was first subjected to a 150 V bias at 315 K and cooled to 200 K when EL intensity approaches its maximum.

A. Device turn on and cooling

Identical 0.6 mm planar LECs on sapphire substrates are turned on by applying a constant 150 V bias at 315 K. EL is typically detected in less than 2 min but continues to increase with increasing doping level and current density. When maximum light output is achieved after about 20–30 min, the device is cooled rapidly to 200 K while maintaining the 150 V "prebias." This leads to a frozen-junction LEC suitable for lifetime study by constant current stress. The turn on and cooling curves of a 0.6 mm planar LEC are shown in Fig. 1, with device current and EL intensity plotted as a function of time. A peak current of nearly 0.3 mA is achieved in this device, which corresponds to a current density of approximately 6 A/cm^2. Both current and EL decrease significantly upon cooling but remain easily detectable at 200 K. All devices studied have similar turn on characteristics.

B. Constant current stress at 200 K

Frozen-junction LECs achieved as described above were subjected to constant current stresses at 5, 10, 20, and 50 μA, respectively. Constant current stress is widely used in lifetime studies where a change in the EL intensity is a direct measure of change in EL efficiency. The driving voltage was also measured to monitor resistance change during the stress.

Figure 2 shows the time evolution of EL intensity (*L*-*t*) in four frozen-junction LECs, each stressed at a different current at 200 K. Since the devices are identical, the initial EL intensity is roughly proportional to the applied current. The EL in all four devices evolves in a similar fashion show-

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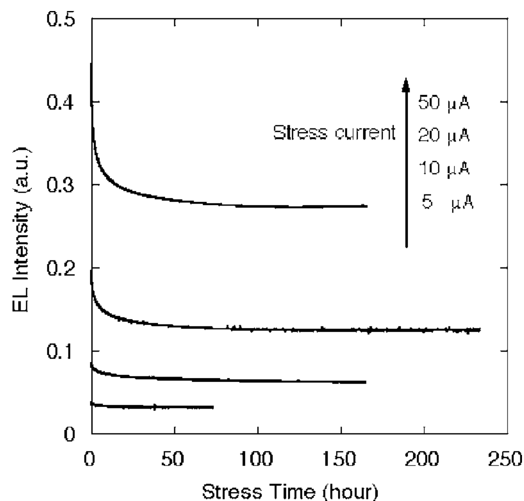

FIG. 2. Time evolution of EL intensity for identical 0.6 mm frozen-junction LECs operated under various currents at 200 K.

ing fast initial decay, followed by a more gradual drop. The decrease in EL intensity under constant current indicates a reduction in absolute EL quantum efficiency. Figure 3 shows the corresponding time evolution of driving voltage (V-t) observed in these devices. The monotonic increase in driving voltage displayed by all devices indicates an increase in device resistance. In addition, the rate of increase is fastest during the initial hours of stress. Unlike EL, the driving voltage is extremely sensitive to fluctuations in temperature (typically less than ±1 K), which is responsible for the noisier look of V-t curves.

An interesting observation is that the EL intensity during the 50 μA stress actually started to increase after 125 h, and the upward trend lasted the reminder of the 165 h stress. Prolonged EL increase during constant current stress was first observed in our initial study of similar devices but occurred much earlier and resulted in a net EL increase of nearly 47% by the end of stress (at 30 μA).[22] This was accompanied by a 54% increase in driving voltage, which is also much larger than the voltage increase experienced by the devices in the current study (less than 4% for 50 μA

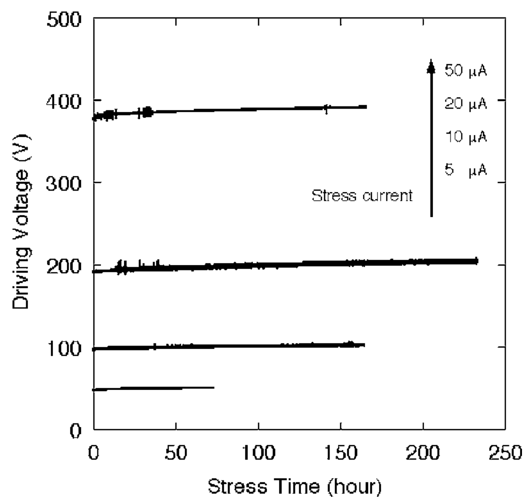

FIG. 3. Time evolution of device driving voltage for identical 0.6 mm frozen-junction LECs operated under various currents at 200 K.

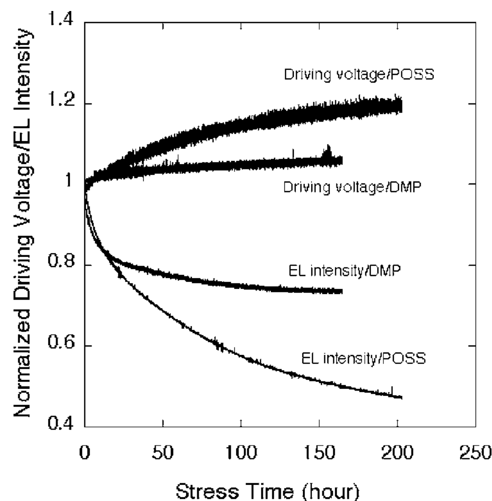

FIG. 4. Time dependence of normalized EL intensity and driving voltage for two 0.6 mm frozen-junction LECs operated at 200 K and a constant current of 10 μA. Both devices are made on sapphire substrates, using polysilsesquioxane (POSS) terminated MEH-PPV and 3,5-dimethyl phenyl (DMP) terminated MEH-PPV, respectively.

stress). Although a net EL increase under constant current indicates an increase in EL quantum efficiency, the earlier devices are, in fact, undesirable due to the fast increase in driving voltage, which translates into a reduced power efficiency of the devices. The dramatic differences observed in these two lifetime studies are quite puzzling since the devices and testing conditions are identical except for two seemingly minor differences: the substrates used (sapphire versus glass) and the end groups of the same luminescent polymer. To find out the effects of these two factors on the degradation of frozen-junction LECs, control experiments were carried out and the results are described in the following two (Secs. III C and III D).

C. The effect of polymer end group on LEC degradation

The luminescent polymers used in both studies are high molecular weight MEH-PPV provided by ADS, Inc., differing only in their end groups. The MEH-PPV used in the previous study is terminated by polysilsesquioxane (POSS) and in the current study terminated by 3,5-dimethyl phenyl (DMP). Figure 4 displays the effects of end group on the stress behavior of planar frozen-junction LECs. Both devices are made on sapphire substrates. The device made with POSS-terminated MEH-PPV is clearly less stable than the device made with DMP-terminated MEH-PPV. After 150 h stress at 10 μA, the "POSS device" has lost 49% of its initial luminance while experiencing a 17% increase in driving voltage. On the other hand, the luminance loss and driving voltage increase of the "DMP device" are only 26% and 6%, respectively. In fact, the POSS device decays much faster than any of the DMP devices shown in Figs. 2 and 3. However, the 17% voltage increase is still much smaller than the 31% voltage increase observed on the POSS device made on glass that underwent the same stress.[22] More importantly, the "POSS-on-sapphire" device shown here does not exhibit the luminance increase observed on all "POSS-on-glass de-

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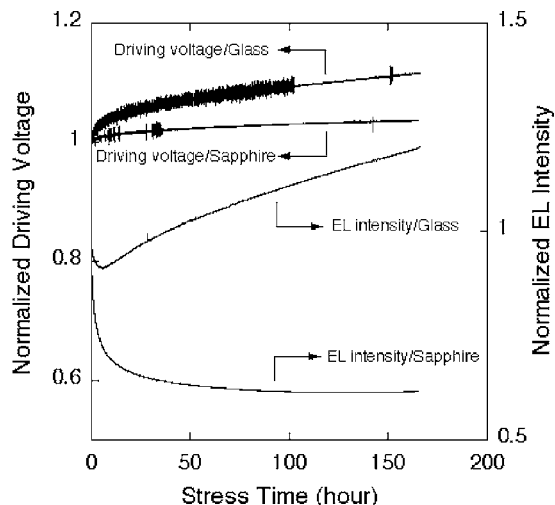

FIG. 5. Time dependence of normalized EL intensity and driving voltage for two 0.6 mm frozen-junction LECs operated at 200 K and a constant current of 50 μA. Both devices are made with DMP-terminated MEH-PPV, one sapphire and glass substrate, respectively.

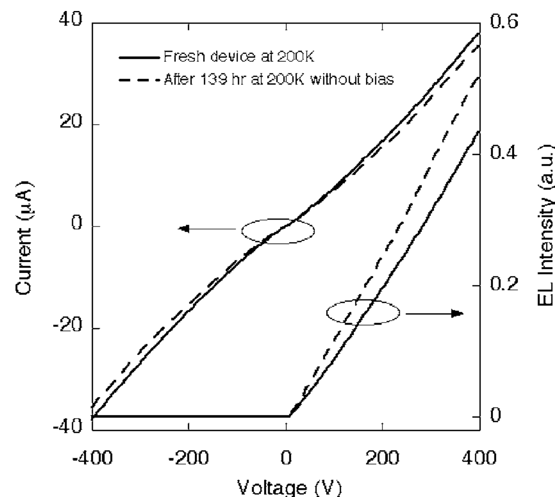

FIG. 6. Current vs voltage and EL intensity vs voltage characteristics of a DMP-on-sapphire device taken at 200 K and 139 h apart. No bias was applied between the scans.

vices." This suggests that the type of substrate must also play an important role in determining the stress behavior of these frozen-junction LECs.

D. The effect of substrate on LEC degradation

Figure 5 compares the degradation of identical DMP devices made on different substrates. The control DMP-on-glass device exhibits dramatically different decay behavior than all DMP-on-sapphire devices shown in Figs. 2 and 3. After 150 h of continuous stress at 50 μA, the driving voltage increased by 11%, compared to only 3.5% for the sapphire device. More significantly, the luminance showed a net increase of 18%, the first observed on a DMP device. The large increase in both driving voltage and luminance is very similar to that observed by all POSS-on-glass devices described in our previous study.

From the results in these control experiments, it is clear that both the end group of the luminescent polymer and the substrate on which the planar device is constructed strongly affect the device degradation characteristics. Since all devices have a planar configuration and all electrodes are deposited on top of the polymer layer, the inert substrates do not play any role in electric injection and transport. However, the substrate affects the heat dissipation and therefore the operating temperature of the device. The frozen-junction LECs are operated at a nominal temperature of 200 K, which is measured off the copper cold finger. The actual device temperature during operation might be significantly higher due to self-heating. The input power used to drive these devices is quite high. For example, the input power for the 50 μA stress (Fig. 5) is initially 17.5 mW and increases with time as the device becomes more resistive. Based on the general heat flow or Fourier equation,[23] the actual device temperature is estimated to be 206.2–206.7 K for devices made on glass substrate.[24] On the other hand, the temperature difference between the cold finger and the device is negligible (less than 0.1 K) for devices made on sapphire substrate due to the much higher thermal conductivity of crystalline sapphire than that of silicate glass.[25] Effects due to substrate heating have also been observed in sandwich LECs by Edman.[11]

E. Evidence of junction relaxation

While elevated temperatures during stress measurements is known to accelerate EL decay and driving voltage increase,[13] the large net luminance increase observed in devices made on glass substrate is quite unexpected. In our previous publication, the luminance increase was explained in terms of electron mobility loss, which can lead to an increased electron capture radius and ultimately more efficient EL if the effect is not dominated by other degradation mechanisms.[22] Although this interpretation was consistent with the predictions of some theoretical models and the observed changes in emission characteristics, the substrate dependence of EL decay and especially the following results suggest an alternative and much more probable explanation of the intriguing phenomenon.

Figure 6 shows the current versus voltage and EL intensity versus voltage scans of a DMP-on-sapphire device taken 139 h apart. The device was stored at 200 K but *not stressed* during the 139 h period between scan. Amazingly, the device also exhibits a large luminance and resistance increase. When EL intensity is compared at the same current of 30 μA, the net increase is 28%, even larger than the 18% increase observed on the DMP-on-glass device stressed at 50 μA (Fig. 5). This suggests that current driven electron mobility degradation is not a necessary condition for luminance increase.

We believe that the luminance increase observed in these frozen-junction LECs is caused by the slow relaxation of the frozen *p*-*n* junction. Recent fluorescence imaging of planar LECs reveals that the polymer film suffers from heavy photoluminescence quenching upon the formation of a *p*-*n* junction via *in situ* electrochemical doping.[20] When left to relax without bias, however, the *p*-*n* junction can relax into a *p*-*i*-*n* junction with a much less quenched quasi-intrinsic

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emission zone formed between *p*- and *n*-doped regions.[7] Controlled doping relaxation by briefly warming the frozen-junction device to elevated temperatures (e.g., 285 K) and then cooling back to 200 K has resulted in a 408% increase in EL efficiency.[26] At 200 K, which is below the glass transition temperature of the PEO electrolyte, the junction relaxation is expected to be much slower. As a result, the observed luminance increase is relatively small.

Doping relaxation also contributes to driving voltage increase as the intrinsic region formed is more resistive. Large driving voltage increases ($>10\%$) have indeed been observed in all devices showing net luminance increase′ after constant current stress. On the contrary, devices that do not exhibit net EL increase (DMP-on-sapphire devices shown in Figs. 2 and 3) display much smaller increase ($<6\%$) in driving voltage. It should be noted that normal current driven degradation also causes the driving voltage to increase as the electron mobility is degraded. This explains the disproportionably small driving voltage increase (4.5%) of the stored device (Fig. 6) compared to its large 28% increase in net luminance at 30 μA, because the current driven degradation mechanism was absent. It is also obvious that normal device degradation dominates the initial stress behavior of all biased devices, when they exhibit fast luminance decay and driving voltage increase. Simultaneous increase in driving voltage and EL intensity (or quantum efficiency) has also been observed recently by Shin *et al.* in micrometer-sized planar frozen-junction LECs subjected to stress. The phenomenon was interpreted in terms of the burnout of doping-induced microshorts.[28] This possibility, however, is ruled out because it cannot explain why similar behaviors were also observed in a frozen-junction LEC that was not subjected to stress, as well as the anomalous trend in driving voltage increase observed in sapphire-based devices.

F. Constant current stress at various temperatures

The effect of doping relaxation is more obvious when planar LEÇs are stressed at higher temperatures. Five identical DMP-on-sapphire devices were turned on at 315 K and subsequently stressed at various temperatures under a constant current of 20 μA. Their *L*-*t* characteristics are shown in Fig. 7 in semilog form. Unlike similar devices stressed at 200 K (Fig. 2), all devices here exhibit pronounced EL increase after an initial decay. In addition, the EL increase occurs earlier with increasing stress temperature. This trend is expected as high temperature promotes ionic motion and therefore doping or dedoping activity. The forward bias applied to maintain the 20 μA constant current obviously cannot prevent the *p*-*n* junction from relaxing into a *p*-*i*-*n* junction, which leads to EL increase and accompanied increase in driving voltage (Fig. 8). The devices stressed at temperatures higher than 250 K eventually underwent catastrophic destruction characterized by a sharp drop in EL intensity and simultaneous fast increase of driving voltage to 1000 V (instrument compliance). The destruction of device is also observed when the device is warmed slowly from below 200 K to above 300 K while under constant current stress.[26]

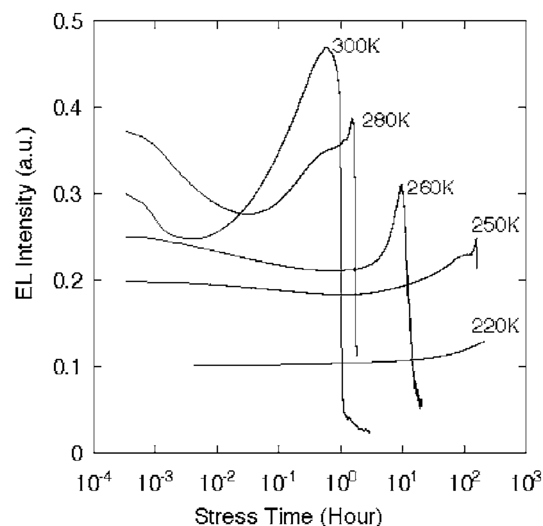

FIG. 7. Time evolution of EL intensity for five identical DMP-on-sapphire devices stressed at a constant current of 20 μA and various temperatures.

G. Lifetime extrapolation

Devices made with DMP-terminated MEH-PPV on sapphire substrates (Fig. 2) are most stable compared to devices made with other combinations of MEH-PPVs and substrates. However, the luminance half-life of these devices cannot be directly determined from Fig. 2 due to the relatively short stress period (limited by cryogen supply). The *L*-*t* curves are well behaved enough to be fitted to a double exponential decay function, as shown by Eq. (1),

$$L_{\mathrm{norm}}(t) = L_{01}e^{-\tau_1 t} + L_{02}e^{-\tau_2 t}, \quad (1)$$

where L_{01} and L_{02} are constants, L_{norm} is normalized luminance, and t is stress time. The curve fits, as shown in Fig. 9, are only performed for the first 50 h of stress to minimize interference from the slow junction relaxation, which causes the *L*-*V* curve to become flat or bend slightly upward. In addition, the data have been normalized and only every 100th of the total data points is shown for clarity (the entire stress consists of nearly 40 000 data points for both *L* and *V*). The "time constants" obtained from the curve fits are listed

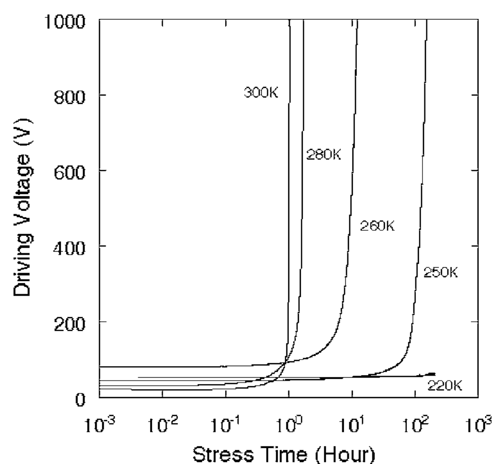

FIG. 8. Time evolution of driving voltage for five identical DMP-on-sapphire devices stressed at a constant current of 20 μA and various temperatures.

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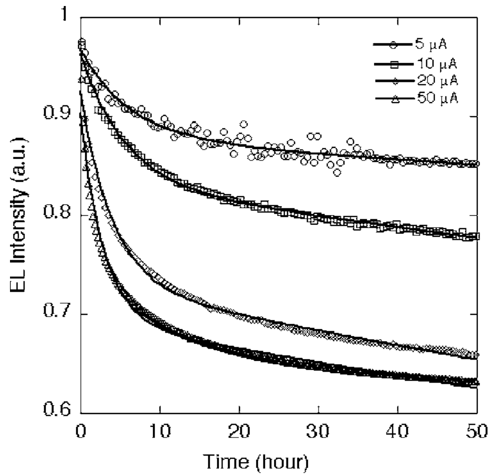

FIG. 9. Normalized EL intensity vs time for devices shown in Fig. 2. The solid lines are double exponential fit.

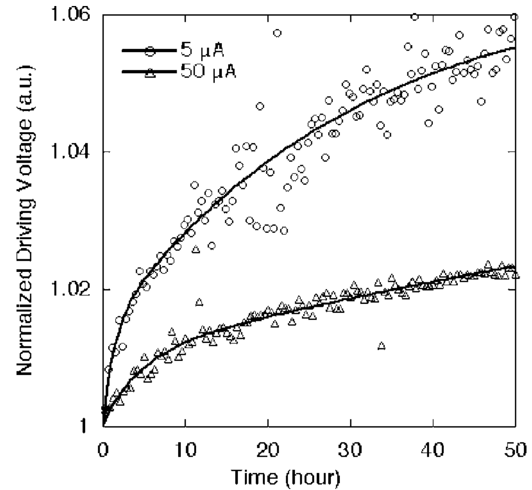

FIG. 10. Normalized driving voltage vs time for identical DMP-on-sapphire devices shown in Fig. 3. The solid lines are double exponential fit.

in Table I. The larger τ_1 is due to the fast initial decay of EL intensity, while the much smaller τ_2 describes the slow decay that follows. Both τ_1 and τ_2 increase with stress current, with the exception that τ_2 obtained at 20 μA is slightly larger than that obtained at 50 μA.

A double exponential fit was also applied to normalized v-t data,

$$V_{\text{norm}}(t) = 1 + V_{01}(1 - e^{-\tau_1^* t}) + V_{02}(1 - e^{-\tau_2^* t}), \tag{2}$$

where V_{01} and V_{02} are constants, V_{norm} is normalized driving voltage, and t is stress time. Again excellent fits are obtained, as shown in Fig. 10. The driving voltage data have a large spread due to temperature fluctuation, and only 5 and 50 μA data are included in Fig. 10 for clarity. Fit constants τ_1^* and τ_2^* are obtained and are also shown in Table I. While the time constants for EL and driving voltage are quite close (τ_1 and τ_1^*, in particular) for high current stress, they are less so for low current stresses at 5 and 10 μA. In fact, stress at the smallest current (5 μA) returned the largest τ_1^* and τ_2^*, indicating the fastest change in driving voltage at this current. On the other hand, the EL decay is slowest at 5 μA with the smallest τ_1 and τ_2. The opposite trend in EL and driving voltage can be directly seen in Figs. 9 and 10. In normal degradation processes present in most polymer or organic LEDs, both EL decay and driving voltage increase are enhanced by high stress current. The anomalous driving voltage behavior observed here can again be attributed to doping relaxation. The forward bias applied to maintain the stress current creates an electrical field in the device, which acts to impede doping relaxation. The average electrical field ($\propto$ applied bias) in the 5 μA stress is approximately 1/8 of that in the 50 μA stress. This leads to faster doping relaxation and the largest voltage increase rate. This argument is supported by the fast doping relaxation observed in devices without bias (Fig. 6) or a negative bias.[27] Although a large stress current may also cause doping relaxation due to local heating, the good thermal conductivity of sapphire as substrate material ensures that this effect is minimal.

Based on current fits for the first 50 h data, luminance half-life for various stress currents are extrapolated and shown in Table II. In agreement with the trend observed in the double exponential fit time constants, the lifetime decreases with increasing stress current.

TABLE I. Double exponential fit constants extrapolated for various stress currents.

Stress current (μA)	Normalized EL intensity		Normalized driving voltage	
	τ_1 (h^{-1})	τ_2 (h^{-1})	τ_1^* (h^{-1})	τ_2^* (h^{-1})
5	0.159	0.000 631	0.748	0.033 4
10	0.179	0.001 38	0.441	0.007 68
20	0.248	0.002 20	0.193	0.006 24
50	0.339	0.002 06	0.227	0.006 15

IV. DISCUSSION

Based on the above observations, we conclude that planar LECs with a preformed p-n junction are highly unstable due to fast doping relaxation when operated at or above 250 K under a constant current. At a nominal temperature of 200 K, however, the stress behaviors are complicated by many competing factors. An increase in stress current results in higher device temperature due to self-heating, which in turn promotes junction relaxation that leads to luminance increase. On the other hand, large (forward) bias and current act to impede junction relaxation and accelerate current-induced luminance decay. Not surprisingly, the thermal conductivity of the substrate plays an important role in determining how the device will behave during stress. The stress behaviors of all devices made on glass are dominated by doping relaxation, as evidenced by the large net luminance increase and fast driving voltage increase. The doping relaxation in this case is mainly caused by substrate heating due to

TABLE II. Extrapolated half lifetimes for various stress currents.

Stress current (μA)	5	10	20	50
Half lifetime (h)	893	386	172	158

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the poor thermal conductivity of glass substrates. As a result, the effect is more pronounced at higher driving current, which causes more heating.

Devices made on sapphire substrates display "normal" decay behavior with increasing driving voltage accompanied by decreasing EL. However, the abnormal trend displayed in the driving voltage again indicates the existence of doping relaxation. The forward bias, which acts to impede doping relaxation, is smallest at 5 μA. This leads to the largest voltage increase rate at this current due to doping relaxation. Overall this "field-dependent" doping relaxation is much weaker than the doping relaxation induced by substrate heating, as observed in devices made on glass substrates. This is consistent with our previous observation of temperature having a much larger effect than electrical field on the rate of ion propagation.[20]

Although the estimated half lifetime of 893 h (5 μA stress) is one of the longest reported for a LEC, it is far shorter than that of polymer LEDs made with the same luminescent material (MEH-PPV), especially considering that these LECs were tested at a much lower temperature. Several factors have contributed to the short extrapolated lifetime. First, the stress current density in these LECs is extremely high due to the small cross-sectional area (0.65 μm $\times$8 mm) of the planar configuration. For example, a 50 μA stress current corresponds to a stress current density of approximately 1 A/cm^2, much higher than that commonly employed in PLED stress measurements (a few mA/cm^2). The actual local current density could be even higher because the electrodes were quasi-one-dimensional and the current density is likely nonuniform. It is well established that the lifetime is inversely proportional to stress current density. In addition, the exponential fit applied to the first 50 h data does not account for the slowing trend in EL decay observed in the latter part of the stress. This is most evident with the 50 μA stress which actually shows slow EL increase after 125 h. While the estimated half-life for this current is only 158 h, the actual EL decrease was less than 40% even after 165 h of stress, indicating that the double exponential fit underestimates the half lifetime. Curve fitting using data for the entire duration gives rise to a half-lie of 700 h for the 50 μA stress. During the 165 h constant current stress at 50 μA, 594 000 C/cm^2 of charge passed through the film. Such high redox stability is comparable to that observed in a PLED with a half lifetime of 20 000 h stressed at 8.3 mA/cm^2.[13]

The large luminance and driving voltage increase displayed by the device stored at 200 K prove that significant doping relaxation can occur even at temperatures below the T_g of the polymer electrolyte used (206 K). While doping relaxation tends to delay luminance decay or even lead to net luminance increase by reducing the PL quenching of the polymer film, it is also responsible for fast driving voltage increase and is therefore undesirable. As a result, we expect stable LEC operation to be only achieved in LECs with a completely frozen junction. Practical LEC applications call for the use of high T_g polymer electrolyte and operation at temperatures well below T_g in order to completely avoid doping relaxation.

V. SUMMARY

The lifetime and degradation characteristics of planar frozen-junction LECs under constant current stress were studied at various temperatures and currents. The devices are shown to be highly unstable when operated at above 250 K. Two seemingly minor parameters, the luminescent polymer end group and the type of substrate on which the device is constructed, have shown profound effects on the stress behaviors of these devices at 200 K. Doping relaxation, accelerated by self-heating and/or lack of forward bias, is responsible for all the anomalous device behaviors observed on both glass and sapphire devices. It is also evident that doping relaxation can occur even at below the glass transition temperature. Devices made on sapphire substrates based on DMP-terminated MEH-PPV are remarkably stable, with an estimated half-life of 700 h when stressed at a current density of 1 A/cm^2.

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