ac Impedance Characteristics and Modeling of Polymer Solution Light-Emitting Devices

Shun-Chi Chang and Yang Yang*
Department of Materials Science and Engineering, University of California at Los Angeles, Los Angeles, California 90095

Fred Wudl
Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles California 90095

Gufeng He and Yongfang Li
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received: May 11, 2001; In Final Form: August 25, 2001

Recently, we demonstrated polymer solution light-emitting devices (SLEDs) using polymeric solutions as the light-emitting medium. The operating mechanism of the SLED was proven to be electrogenerated chemiluminescence (ECL). In this manuscript, we report the results obtained from ac impedance studies on the SLED. Based on the results, the SLED can be modeled as a combination of device capacitance ($C_1$), solution layer resistance ($R_1$), interfacial capacitance ($C_2$), and interfacial resistance ($R_2$). It was found that the impedance characteristics of the SLED are a strong function of the bias voltage. At low bias voltages, the impedance plots exhibited semicircular and linear characteristics in the high- and low-frequency range, respectively. With increase in the bias voltage, $C_2$ decreased, implying an ECL mechanism for the SLED. Finally, an interesting behavior was observed when the SLED was biased at 8 V. The impedance spectrum was similar to that of the solid-state polymer light-emitting electrochemical cell (LEC), suggesting some similarities in the device operating mechanism between the SLED and LEC.

Introduction

Electroluminescent polymers and polymer light-emitting devices such as light-emitting diodes (LEDs)$^{1,2}$ and polymer light-emitting electrochemical cells (LECs)$^{3,4}$ have drawn much attention since 1990. Recently, a new type of polymer light-emitting device, the polymer solution light-emitting device (SLED), was demonstrated.$^5$ In the SLED, a layer of luminescent polymer solution is sandwiched between two indium tin oxide-coated (ITO) glass electrodes and serves as the light-emitting medium. An electrogenerated chemiluminescence (ECL) mechanism, based on the interaction of radical ions of n-type and p-type molecules, was proposed to explain the light emission. When an electrical bias is applied to the SLED, radical cations (for example, solvent molecules) and radical anions (for example, polymer molecules) are produced near the anode and cathode, respectively. The radical ions with the lower molecular weight and relatively higher mobility migrate and transfer their charge to their oppositely charged counterparts, typically the luminescent polymer which is relatively immobile. This results in the formation of an excited state of the luminescent molecules. Light emission occurs when the molecules in the excited state radiatively decay to their ground state (eq 1):

$$A^{*} + B^{*+} \rightarrow A^{*} + B \text{ or } A + B^{*} \rightarrow A + B + h\nu$$

(1)

where A and B are the species that are easily reduced and oxidized, respectively. The ECL mechanism was also supported by the surface cell experiments of the SLED.$^6$

However, the electronic property of the SLED has not been carefully investigated. Electrochemical impedance spectroscopy (EIS) has been used successfully in the past for the elucidation of the electronic structures of the LECs$^9,10$ and polymer LEDs$^9,11,12$ and was used in this research to clarify the electronic property and explain the model for the equivalent circuit of our SLED. An attempt was then made to verify this model by making approximations in the high- and low-frequency ranges and also by studying cells with different thickness. In this work, voltage-dependent impedance characteristics of the SLED have also been investigated and reported. It is very interesting to see that the SLED behaves similar to a solid-state polymer LEC at high bias voltages. This observation suggests the possibility of electronic hopping within polymer chains near the interface.

Experimental Section

The fabrication processes of the SLED has been described in detail elsewhere.$^5$ The SLED was prepared by sandwiching the luminescent polymer solution between two ITO-coated glass electrodes. The thickness of the polymer solution was controlled by embedding glass beads within the edge-sealing epoxy. The glass beads used ranged from 1 to 2 µm in diameter for the regular SLEDs. However, glass beads ranging from 10 to 100 µm diameter were also used to increase the thickness of the solution layer. The glass beads were blended with UV-curable epoxy having a low viscosity. The epoxy blend was deposited on the edge of one ITO/glass substrate. The second ITO/glass substrate was subsequently placed on top of the first ITO/glass substrate. The cell thickness was fixed after the UV-curing...
Results and Discussion

drawn to analyze the impedance results.

Figure 1. Nyquist plots of ITO/PF+DCB/ITO SLED at different bias voltages: (a) 0 V; (b) 2 V; (c) 3 V; (d) 4 V. The inset shows the Nyquist plot at 0 V.

The process is completed. The polymer solution was later filled into the cell by capillarity. The luminescent polymer solution in the SLEDs was 5% poly [9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] (BDOH-PF) in 1,2-dichlorobenzene (Aldrich, anhydrous, 99%). The salt added to the polymer solution, wherever indicated, was tetra-n-butylammonium hexafluorophosphate (Fluka, electrochemical grade). In this manuscript, our device is abbreviated as ITO/PF+DCB/ITO for convenience. The ac impedance was measured with a HP 4284A Precision LCR Meter in the frequency range from 20 Hz to 1 MHz, and the amplitude of the ac signal used was 20 mV. The impedance results in this paper are expressed as

\[
Z = Z' - jZ''
\]

where, \(Z'\) and \(Z''\) are the real and the imaginary part of the impedance, respectively. Nyquist plot (the plot of \(Z''\) to \(Z'\)) and Bode plot (the plot of \(\log Z''\) to \(f\), where \(f\) is the frequency of the ac signal used in the ac impedance measurement) were drawn to analyze the impedance results.

Results and Discussion

ac Impedance Spectroscopy and Equivalent Circuit. Figure 1 shows the impedance plots (Nyquist plots) of the imaginary part (\(Z''\)) to real part (\(Z'\)) of the regular SLED at different voltages ranging from 0 to 4 V. At bias voltages of 0 and 2 V, the impedance plots exhibit a semicircular characteristic in the high-frequency range and a linear behavior in the low-frequency range. However, at a bias voltage of about 3 V, which is more or less equal to the charge injection voltage [calculated from the potential difference (\(V_d\)) between the oxidation and reduction potentials], the impedance plot changed dramatically. The diameter of the semicircle in the higher-frequency range increased and the slope of the straight line in the lower-frequency range decreased. At about 4 V, both the semicircle and the straight line were replaced by a new curve. In addition, it can be seen that the contacts are ohmic, which is different from the impedance spectra of PLEDs and OLEDs.

On the basis of the device structure, which consists of polymer bulk solution and interfaces between the ITO and polymer solution, the equivalent circuit for our device structure may be depicted by a parallel combination of \(C_1\) and \(R_1\) in series with a parallel arrangement of \(C_2\) and \(R_2\), as shown in Figure 2. \(C_1\) and \(R_1\) represent the device capacitance and the resistance, respectively, of the solution layer in the device. \(C_2\) and \(R_2\) represent the capacitance and resistance of the interface between the ITO electrode and the solution layer, respectively. When the dc voltage is 0 V, \(C_2\) should be much larger than \(C_1\) due to the much smaller thickness of the interface compared to the polymer solution. Consequently, in the high-frequency range at 0 V, the impedance \(C_2\) can be neglected due to its high capacitance \([Z = -j/(1/2\pi fC)]\) for a capacitor \(C\) and the semicircle in Figure 1 should correspond to the parallel circuit of \(C_1\) and \(R_1\). The device resistance \(R_1\), calculated from the diameter of the semicircle at 0 V (inset in Figure 1), is ca. 2 kΩ. In the lower-frequency range, on the other hand, the impedance of \(C_1\) is very large with respect to \(C_2\), and the equivalent circuit should be \(R_1\) in series with the parallel circuit of \(C_2\) and \(R_2\).

Calculation of Capacitances from Bode Plots. To analyze the capacitance values, Bode plots, which mean the logarithmic plots of impedance to frequency, were plotted as shown in Figure 3. It can be seen that the two Bode plots at 0 and 2 V are almost identical. In these two plots, the value of the imaginary part, \(Z''\), first decreased at low frequencies, passed through a minimum, subsequently increased, reached a maximum, and then decreased at high frequencies. With the increase in voltage from 2 V to 4 V, both the minimum and the maximum shifted to lower frequencies and the respective \(Z''\) values increased, indicative of the increase of the semicircle diameter and thus the increase in the corresponding resistances. However, at the higher voltages (4 V − 6 V), the Bode plot is completely different. The maximum shifted to a much lower frequency, and the minimum in the low-frequency range disappeared. In addition, in the plot without bias, there are two straight lines with a slope of ca. −1 in the high- and low-frequency range, respectively. From the two straight lines, \(C_1\) and \(C_2\) were calculated to be 0.3 nF and 200 nF, by applying the formula \(Z = (1/2\pi fC)\) in the high- and low-frequency ranges, respectively. The value of 0.3 nF is lower than capacitance of solid-state thin-film PLEDs, which are about 2 nF. This can be attributed to the SLED thickness, which is about an order of magnitude greater than the PLED.

To further verify the values of \(C_1\) and \(R_1\) obtained earlier, two sets of ac impedance measurement experiments were
the devices is (a) ca. 10 μm, (b) ca. 2 μm.

The other set was obtained for a SLED with salt added into the polymer solution. Figure 4 shows the impedance plots of the SLED at zero voltage, the thickness of device resistance $R_1$ for the blend observed in Figure 5 is

\[ R_1 \approx 11 \text{ kΩ} \]

from the two straight lines of the Bode plot for this device at 0 V in Figure 4b, $C_1$ and $C_2$ were calculated to be ca. 0.07 nF and 200 nF, respectively. In addition, the shift of $C_2$ value of 5 and 6 V. At this voltage, instead of one semicircle and one straight line, only one new curve exists. This result indicates that $C_2$ decreases with the increase of the bias voltage and is comparable to $C_1$ when the voltage is higher than 4 V. This scenario would prevail when the interface thickness becomes similar to the device thickness as can be seen from eq 3:

\[ C = \epsilon \epsilon_0 A / d \]  

Figure 5. Nyquist plot of the SLED with TBAHP at 0 V. The inset shows the Nyquist plot at the frequency range from 1 MHz to 30 kHz.

these blends as the active medium, not only lowered photoluminescence, but also resulted in higher device currents. The latter is due to the increase in the conductivity by chemical doping, as is observed in conducting polymers such as 3,4-polyethylenedioxythiophene-polystyrene sulfonate (PEDOT).14 All the results mentioned above verify the fitness of the equivalent circuit in Figure 2.

Voltage Dependence of ac Impedance and Electronic Structure of SLED. It can be observed from Figures 1 and 3 that the ac impedance of the SLED is voltage dependent between 0 and 6 V. Further from Figure 1, the impedance plot at bias voltages less than 3 V is very similar to that at 0 V except that the straight line in the lower-frequency range bends slightly, due to the slight decrease in $R_2$ ($R_1$ might be voltage dependent). At bias voltages higher than $V_d$ (≈3 V), the impedance plots, both Nyquist and Bode plots, are completely different. It can be seen in Figure 3 that the straight line in the lower-frequency range, which corresponds to the impedance of $C_2$, moves upward with increasing voltage from 2 to 5 V, and almost overlaps with the straight line in the higher-frequency range at the bias voltages of 5 and 6 V. At this voltage, instead of one semicircle and one straight line, only one new curve exists. This result indicates that $C_2$ decreases with the increase of the bias voltage and is comparable to $C_1$ when the voltage is higher than 4 V. This scenario would prevail when the interface thickness becomes similar to the device thickness as can be seen from eq 3:

\[ C = \epsilon \epsilon_0 A / d \]  

in which $\epsilon$ is the dielectric constant of polymer solution, $\epsilon_0$ is the vacuum permittivity, $A$ is the contact area, and $d$ is the thickness. This phenomenon can be interpreted by means of the device electronic structure shown in Figure 6. When the applied voltage is lower than the charge injection voltage ($V_d$), for example 2 V, there are only a few ions generated in the solution due to oxidation and reduction, as shown in Figure 6a. As the ac voltage is applied on the device in the ac impedance measurement, some polarized counter charges will be induced in the solution only near the interface between the polymer solution and the ITO electrodes. This would result in a large interface capacitance $C_2$ at 0 V and at 2 V and no change in the diameter of the circle (i.e., no change in the solution resistance $R_1$), which is consistent with the proposed equivalent circuit in Figure 1. When the bias voltage is higher than 3 V, radical anions of the luminescent polymer, BDOH-PF are
generated near the cathode. Simultaneously, the radical cations of DCB solvent molecules are produced by oxidation reactions at the anode side. Because of their large size and relatively low mobility BDOH-PF, BDOH-PF radical anions accumulate near the cathode side. On the other hand, DCB radical cations accumulate and diffuse toward the counter electrode. This phenomenon of charge distribution is depicted in Figure 6b. As a result, the ITO/solution interfacial layer becomes wider, resulting in the decrease of the interface capacitance \( C_2 \), as shown in the Bode plots in Figure 3. In addition, unlike solid-state PLEDs where the diameter of the semicircle starts to decrease at voltages greater than device turn-on voltage, \( V_T \), the Nyquist plots of the SLEDs begin to vary significantly at the charge injection voltage \( V_0 \).

In Figure 3, it can be seen that \( C_1 \) is independent of the applied dc voltage; however, \( C_2 \) decreases with the increase of dc voltages, as discussed above. In addition, when the value of \( C_3 \) is similar to that of \( C_1 \), the semicircle cannot be differentiated from the straight line and they merge into one curve. According to eq 3, \( C_1 \) is almost identical under different voltages due to the fixed bulk thickness of the device. On the other hand, the thickness of interface will increase with increase in the applied voltage. Therefore, the value of \( C_3 \) will decrease with the increase in \( d \) according to eq 3. A clearer picture is obtained in the thicker SLED with a thickness of 10 \( \mu m \), as shown in Figure 7. Compared to Figure 1, the impedance spectra of the thicker device still comprises two curves at 6 V. When the applied dc voltage is higher than 10 V, the two curves cannot be differentiated. This result implies two discrete regions, i.e., bulk and interface exist at low voltages, will merge into one at higher voltages, which is higher (i.e., 10 V) for the 10 \( \mu m \) thick SLED as compared to the thinner SLED.

**Charge Hopping at Voltages Higher than 8 V.** When the voltage is higher than 8 V, the impedance for a 2 \( \mu m \) thick SLED behaves quite differently from that at lower voltages, as shown in Figure 8. The Nyquist plots show a flattened semicircle and the diameter of the semicircle decreases with increasing voltage, which is similar to the impedance behavior of a polymer LEC. It is quite likely that this is because of electron and hole injection directly into the BDOH-PF conjugated chains followed by charge transfer between the conjugated chains under the high electric field. In addition, the flattened semicircle might also result due to the ionic effects in the polymer solution layer.

**Variation of Device Resistance** \( R_1 \) **and Interface Resistance** \( R_2 \). It can be seen from the inset of Figure 1 that the straight line in the impedance plot at 0 V is almost perpendicular to the \( Z' \) axis, indicating that \( R_2 \) is very large at 0 V. With the increase of voltage (0–4 V), \( R_1 \) increases but \( R_2 \) decreases, as shown in Figure 1. When the voltage is higher than 5 V, the interface thickness increases and equals the device thickness. As a result, the diameter of the semicircle represents the total resistance \( R_T \), which is the summation of \( R_1 \) and \( R_2 \). In general, \( R_T \) increases with the increase in voltage from 3 V (\( V_0 \)) to 6 V. At voltages higher than 8 V, \( R_T \) decreases as shown in Figure 8. This result can be interpreted as follows: The variation of resistance not only depends on the applied dc voltages but also on the charge accumulation at the interface. The increasing voltage would facilitate the charge transfer at the interface leading to a decrease in the value of \( R_T \). On the other hand, the charge accumulation with the increase of voltages makes further charge injection difficult, resulting in the increase in the value of \( R_T \). Therefore, in the voltage range 3–6 V, charge accumulation may be a serious problem, and thus \( R_T \) increases with the increase of voltage. When the applied voltage is higher than 8 V, charge hopping under the high electric field occurs to reduce the charge accumulation at the interface, resulting in the decrease of the resistance, \( R_T \).

**Conclusion**

The electronic structure of the SLED was investigated by the measurements and analysis of ac impedance. An equivalent circuit was proposed to model the device electronic structure.
The characteristics of the SLED impedance indicate that the mechanism of the light emission depends on the bias voltage. When the voltage is higher than $V_d$ (potential difference required for the oxidation and reduction of the respective species) but lower than the voltage for direct charge injection and charge hopping between the conjugated chains ($V_2$, such as 8 V), light emission comes from the ECL mechanism. When the voltage is higher than $V_2$, electron and hole injection into the conjugated chain and their subsequent recombination will be responsible for the light emission.

**Acknowledgment.** This work is supported by a research grants AFOSR (F49620-00-1-0103), and the discussions with Dr. Qibing Pei at SRI are greatly appreciated.

**References and Notes**


