

Capacitance–voltage characterization of polymer light-emitting diodes

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The capacitance–voltage (C – V) characterization of polymer light-emitting diodes (PLEDs) employing poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene], as the light-emitting layer are reported. Several metals, such as calcium (Ca), aluminum (Al), and gold (Cu) were used as the cathode in order to investigate the influence of the charge injection on the C – V characteristics. Under forward bias, the capacitance increases with majority charge carrier injection into the polymer layer, and, afterwards, decreases upon minority charge carrier injection which results in recombination of electrons and holes in the active polymer layer. The increase in the value of capacitance follows the same dependence as the increase in the value of current density through the device, which suggests that the capacitance depends not only on the amount of charge trapped in the polymer near the interface, but also, and mainly, on the amount of charge injection into the polymer layer from the electrodes. The C – V behavior of PLEDs with added amount of ionic defects was also studied. The capacitance values are higher for devices with higher amount of added impurities in form of ionic electrolytes, and, the increase in the capacitance under forward bias also depends on the ionic defect concentration. © 2005 American Institute of Physics.

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I. INTRODUCTION

Polymer light-emitting diodes (PLEDs) (Ref. 1) have been recognized as a promising technology for flexible displays.^{2–4} A PLED with high quantum efficiency requires efficient dual carrier injection and transportation in order to achieve electron and hole balance.^{5,6} The charge injection and transporting mechanisms and the organic-metal interface of PLEDs have been extensively studied and reported.^{7–11} The interest in PLEDs for solid state lighting has been renewed with the recent report of ultrahigh efficiency LEDs, with efficiency as high as 28 Cd/A.¹²

In this paper we report the capacitance–voltage (C – V) characteristics of PLEDs and relate the behavior of C – V characteristics to the onset of majority and minority charge carrier injection into the active polymer layer from the electrodes. In the past, C – V and ac impedance characteristics of PLEDs (Refs. 13–15) and polymer light-emitting electrochemical cells (LECs) (Refs. 16 and 17) have been reported, but those have mainly focused on reverse bias and low forward bias conditions. Campbell *et al.*¹³ reported C – V characteristics of PLEDs in low forward bias and suggested that charging of traps near the metallic contacts results in increase in the capacitance of the diode. In our measurements we observed the capacitance variation in large forward bias (higher than the device turn on voltage) to be dependent on the type of cathode used as the top contact. Also the relative increase in the value of capacitance and the bias associated with the dramatic increase and decrease in the capacitance values are also dependent on the carrier injection. By comparing the C – V curves to the current–voltage (I – V) curves,

we have shown that the change in capacitance is due to the majority and minority charge injection from electrodes into the polymer.

II. EXPERIMENT

The PLEDs were fabricated using poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene], MEH-PPV, as the semiconducting, electroluminescent polymer. The devices were fabricated on the glass substrates precoated with indium tin oxide (ITO). The polymer was spun-cast from cyclohexanone solution (10 mg/ml) onto these substrates; the typical thickness of the polymer film being about 1000 Å. Calcium (Ca), aluminum (Al), and gold (Au) were used as the different electron injecting electrodes (cathode), vacuum evaporated (in 10^{-6} Torr vacuum) on top of the polymer films. The final structure of the devices was ITO/PEDOT:PSS/MEH-PPV/Cathode. All the devices were fabricated and tested in nitrogen atmosphere. The I – V characteristics for the devices were measured by using a Keithley 2400 source measure unit. The capacitance and the ac impedance measurements of the devices were conducted at the room temperature in the dark, using a HP 4284A LCR Precision Meter. The complex ac impedance measurements were done in Z – θ mode for a varying frequency (f), from 20 Hz to 1 MHz with an ac drive bias of 30 mV. A constant dc bias was applied ranging from 0 V to ± 3 V, superimposed on the ac bias. For the capacitance–voltage measurements, the devices were biased from 0 V to ± 3 V with voltage steps of 0.05 V, superimposed on top of an ac drive voltage of 30 mV and a constant frequency. The C – V curves were acquired for different constant frequencies ranging from 100 Hz to 1 MHz. The C – V data was acquired by using a LABVIEW® program, controlling the LCR meter

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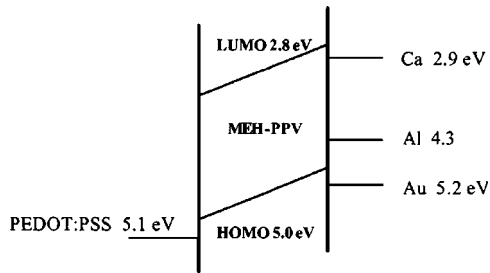


FIG. 1. Band diagram model of PLED showing the relative positions of Fermi energies for metals and PEDOT:PSS and HOMO and LUMO positions for MEH-PPV.

through GPIB interface. For all the cases of applied bias, the ITO electrode was biased positive and the metal electrode as negative.

III. RESULTS AND DISCUSSION

Figure 1 represents the band diagram model of our PLEDs showing the Fermi level positions for various materials that were used to make our devices. As is visible from the band model, the increasing offset between the Fermi energy level of the metal cathode and the LUMO level in MEH-PPV will result in reduced level of electron injection from the cathode into the polymer layer, and the injected holes will be the dominant charge carriers when Al and Au are used as the cathode, making the devices increasingly single carrier “hole-only.” The holes injected from PEDOT:PSS layer will be the dominant charge carriers, and the current in the device is controlled almost exclusively by the holes. On the other hand, the devices with Ca as the electrode will be double carrier devices. The current–voltage curves for these three kinds of devices in forward and reverse bias are shown and compared in Fig. 2. Using different metals, and thereby controlling the amount of electron injection into the polymer from the cathode, provides an opportunity to study the role of charge carrier injection on the capacitance of the device as a function of applied bias during the device operation.

Figures 3(a) and 3(b) show the normalized capacitance (C/C_0) for the devices at 100 Hz, with different metal cathodes, as a function of the bias voltage (here C_0 is the capacitance of the device at zero bias). As seen from Fig. 3(a), the

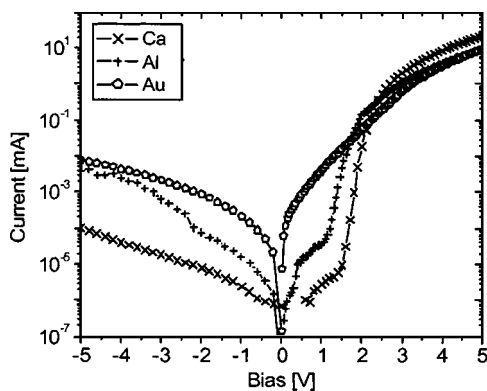


FIG. 2. Current density as a function of applied bias (forward and reverse) for PLEDs with different metal electrodes (Ca, Al, Au).

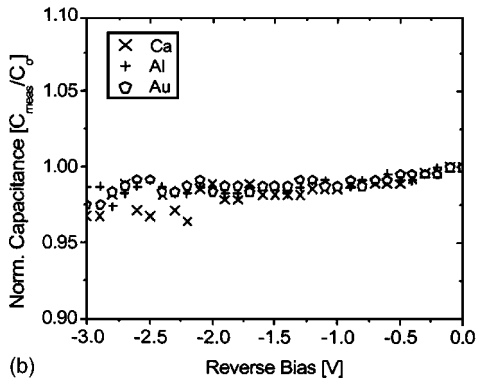
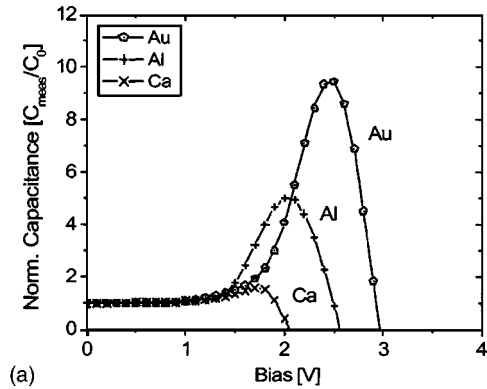


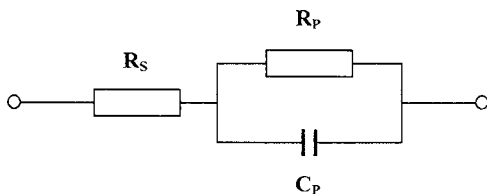
FIG. 3. Normalized capacitance measured for PLEDs with different metals as cathodes (a) in forward bias, and, (b) in reverse bias.

capacitance of all the devices increases in forward bias till a point where it reaches a maximum value, and decreases sharply after that. This is in accordance with the previously reported results by Campbell *et al.*¹³ Additionally, the figure shows that the onset voltage of the increase and the roll-back in capacitance depends on the metal used as the cathode for each device. The increase in the capacitance was more pronounced for the device which has a higher work function metal as the cathode, or in other words, the capacitance increased most for the devices with Au as the cathode, followed by Al, and Ca. This suggests that the capacitance of PLEDs under forward bias maybe dependent on the charge injection across the metal/polymer interface. From Fig. 3(b) it can be seen that the value of capacitance remains almost constant during applied reverse bias.

To explain this phenomenon, we propose a simple explanation for the origin of capacitance in PLEDs. At zero bias, the capacitance of the device is same as the geometrical capacitance, $C_0 = \epsilon \epsilon_0 A/d$,¹⁷ where ϵ , ϵ_0 A and d are relative dielectric constant of the polymer, permittivity of the free space, area of the device and the thickness of the polymer film, respectively. The constant capacitance of a PLED at reverse bias suggests that there exists a depleted region across the polymer film in the device, which in turn suggests that the device has a flat band structure in reverse bias.⁷ On applying a small forward bias, there is no apparent change in the value of capacitance, and it remains equal to C_0 , the geometric capacitance described above which is because of the dielectric properties of the polymer.¹⁴ This capacitance remains almost constant until a point where the majority charge (holes, in this example) injection begins from the an-

ode. This majority carrier injection marks a sharp increase in the capacitance (Fig. 3). On further increasing the bias, the minority charge injection occurs, which results in recombination of electrons and holes in the polymer and emission of photons and the amount of charge that is present in the polymer decreases significantly. This explains the decrease in the capacitance at a higher bias. This decrease in capacitance is not only because of the neutralization of trapped charges as suggested by Campbell *et al.*,¹³ but mainly because of the recombination of electrons and holes, resulting in decrease in the amount of charges present in the polymer significantly. The above assumption is supported by the fact that the relative increase in the capacitance is more for the device with a higher work function metal as the cathode. While the onset voltage of majority charge injection from the anode (holes) is same for all the devices and independent of the kind of cathode selected, the minority injection from the cathode (electrons in this case) will take place at a much higher bias when the cathode has a higher work function. Until that point the charge accumulation in the polymer will keep on increasing, thereby increasing the capacitance. Also the bias at which capacitance starts decreasing is lowest for devices with Ca as the cathode, and highest for Au, which again can be explained by the fact that a higher bias is required for minority charge injection, in case of devices with higher work function cathode.

It has been reported that PLEDs behave like a pure capacitor for low applied bias,¹⁶ but for a dc bias higher than the energy gap of the polymer (2.1 eV for MEH-PPV in this case) the Z'' vs Z' plot of PLED is a semicircle with a small tail at low frequencies. The complex impedance of the device, Z can be expressed as $Z = Z' - jZ''$, where Z' is the real part and Z'' is the imaginary part of the complex impedance.¹⁷ In order to explain the complex impedance of the device, the equivalent circuit of a PLED is shown below, consisting of a capacitor (C_p) and a resistor (R_p) in parallel in series with a resistance (R_s).



The complex impedance, along with the real and imaginary part, of the above circuit is expressed as below:

$$Z = R_s + \frac{R_p - j\omega R_p^2 C_p}{1 + \omega^2 R_p^2 C_p^2}$$

$$Z' = R_s + \frac{R_p}{1 + \omega^2 R_p^2 C_p^2}, \text{ and } Z'' = \frac{\omega R_p^2 C_p}{1 + \omega^2 R_p^2 C_p^2}$$

Figure 4 shows the Cole-Cole plot for PLEDs with Ca, Al, and Au as the cathode for an applied forward bias of 3 V. The Z'' vs Z' curves with frequency as the implicit variable are semicircle for all three devices. This suggests that both C_p and R_p are independent of the frequency for a forward bias as high as 3 V.

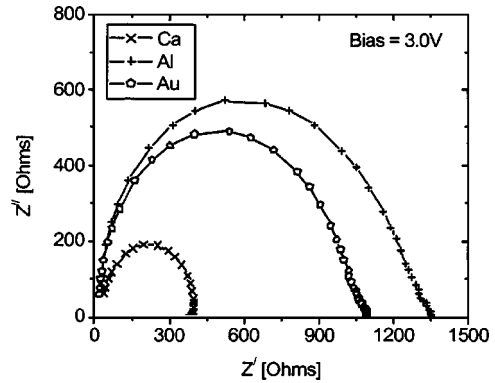


FIG. 4. Cole-Cole plots (Z'' vs Z') with frequency as the implicit variable for PLEDs with Ca, Al, and Au as the cathode at a forward bias of 3 V.

Figure 5 shows a typical $C-V$ curve for a PLED and four distinct regions are marked in the figure corresponding to neutral regime, dark current regime, majority charge-injection regime, and charge recombination regime. The voltage V_1 is the bias voltage at which the majority charge injection into the polymer, holes in this case, starts in forward bias. Below this voltage the polymer is basically neutral with a very small amount of charge trapped in the defect sites near the interface. The polymer layer can be thought of as composed of small charge regions near the interface and a large neutral region elsewhere. The capacitance now is the geometric capacitance due to the dielectric properties of the polymer layer, as explained above. Above V_1 , a sharp capacitance increase is observed corresponding to the majority charge injection as explained above as well. The voltage V_2 corresponds to the device-turn on voltage, at which the light emission from the polymer begins and marks a sharp decline in the value of the measured capacitance of the device. It should be noted that both V_1 and V_2 lie below 3 V and the capacitance and the resistance components of the impedance are independent of the frequency at these bias points as explained on the basis of the Cole-Cole plot in Fig. 4.

In order to study the relationship between the charge injection and the capacitance, it is important to understand the behavior of current density and capacitance change between voltages V_1 and V_2 for our devices. The values of V_1

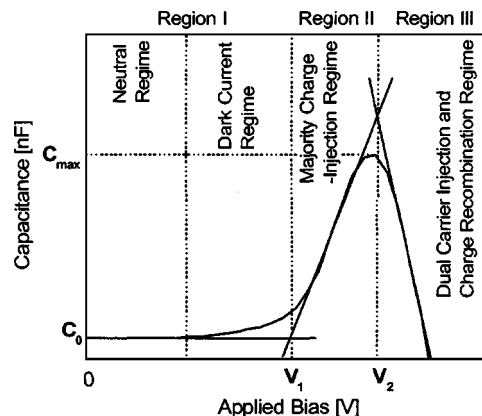


FIG. 5. A typical $C-V$ curve for a PLED device under forward applied bias shows three distinct regions corresponding to the amount of charge present in the polymer film.

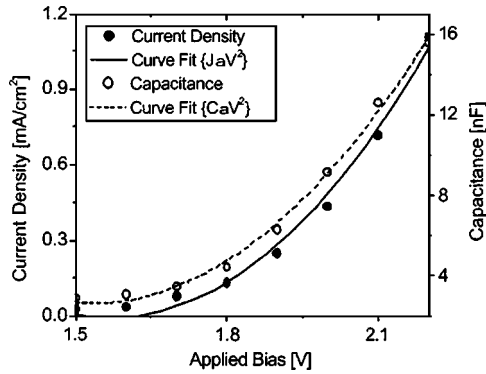


FIG. 6. Measured values of current density and capacitance for a typical PLED with Al cathode, for applied forward bias between V_1 and V_2 and curve fit according to the SCLC model.

and V_2 for Al devices are found to be 1.4 V and 2.4 V, respectively. The dependence of current density, J , on the applied bias, V , for semiconducting polymers has been explained by several models, of which space-charge limited current (SCLC) model^{18,19} is widely accepted. According to the SCLC model, the relation between J and V is given by $J \propto V^2$.¹⁹ Figure 6 shows the measured current density and capacitance values between V_1 and V_2 for the device with an Al cathode. As can be seen from the figure, the curve fit according to $J \propto V^2$ matches well with the measured values of current density. Also the measured values of capacitance, C , fit well according to $C \propto V^2$. The fact that both current density and capacitance depend on the square of applied bias proves that the capacitance increase between V_1 and V_2 can be attributed to the majority charge injection into the polymer.

This explanation is further supported by observing the current-light-capacitance curves as a function of the applied forward bias for the three different devices, as shown in Figs. 7(a)–7(c). The bias where capacitance starts decreasing is observed to be same as the device turn-on voltage, at which the light emission from the device is observed. This is observed for all the three different devices, with Ca, Al, and Au as the cathodes. This clearly suggests that the capacitance in single carrier devices not only depends on the space charge, but also on the recombination, just like in case of double carrier devices, even though the amount of recombination is significantly less in single-carrier devices. The forward bias capacitance behavior of our diodes is very different from the reverse bias behavior. In reverse bias the junction capacitance is the dominant, whereas in case of forward bias, diffusion capacitance is dominant. C – V curve for our device suggests that PLED is a short-base diode where the minority charge carrier diffusion lengths are much longer than the length of the diode. The current-voltage dependence of a PLED is different from an inorganic diode because the current is space charge limited. This suggests that the increase in the capacitance for PLED is not necessarily exponential, but proportional to square of V , similar to J – V dependence in the SCLC model. This gives us an opportunity to compare and differentiate PLED from the inorganic p – n junction.

The measurement of junction capacitance is often used as a tool to determine the doping concentration in

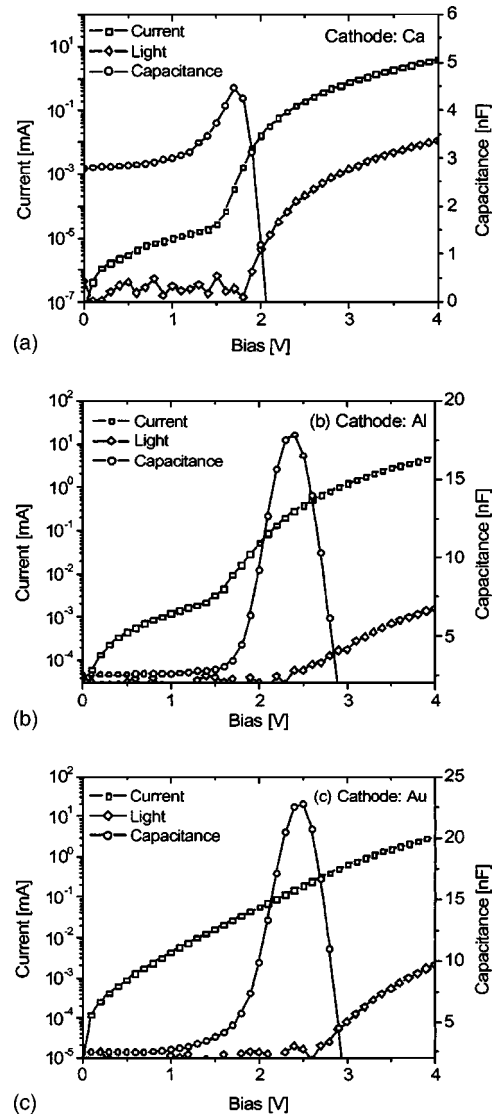


FIG. 7. Current-light-capacitance curve for MEH-PPV based PLEDs with Ca, Al, and Au as metal electrodes.

junctions.²⁰ Therefore the ac impedance measurements were performed on the devices, with the goal of detecting impurities through C – V characteristics. For this purpose, we purposely added salt impurities into highly purified MEH-PPV polymer to be used as the active layer in the device. The current-voltage (I – V) characteristics of the PLEDs with different amount of salt concentrations in the polymer are shown in Fig. 8(a) in forward and reverse bias. An increase in the reverse bias current with the increase in the amount of salt present in the polymer agrees well with the fact that the salt, which is present in the polymer as ionic impurity, contribute more to the ionic conduction, in addition to the charge conduction because of the charge already present in the polymer, thereby increasing the dark current. This degradation in device performance with increasing salt concentration is also reflected in the electroluminescence (EL) brightness and EL efficiency measurements. The EL-voltage and the EL quantum efficiency measurements for the devices are shown in Fig. 8(b).

In order to further study the effect of ionic impurities

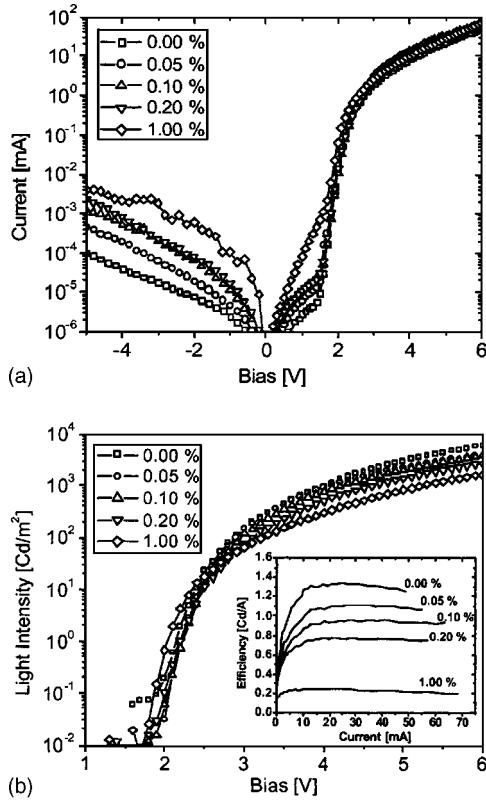


FIG. 8. I - V characteristics of ITO/PEDOT/MEH-PPV/Ca PLEDs with a different amount of ionic salt impurities (LiCF_3SO_3) added to the polymer.

present in the device and the role they play while the device is biased, the capacitance measurements were done on PLEDs with varying salt concentration. The capacitance was calculated from the measured complex impedance Z and the phase angle θ , as follows:

$$C_P = -\frac{\sin(\theta)}{2\pi f \times |Z|},$$

where, f is the frequency, and $|Z|$ is the modulus of complex impedance Z .

Figure 9 shows the C - V characteristics for a device with no added salt (a), and for a device with 0.20 wt. % salt (b), in the polymer for frequency range of 100 Hz–100 kHz. For all applied frequencies, the capacitance of the PLED increases with bias, when the devices are biased in the forward direction, attains a maximum value and then decreases sharply thereafter. In the reverse bias the capacitance of the device remains almost constant for all the frequencies. The absolute value of capacitance is higher, for a given device at a given applied bias, for lower frequency and it decreases with increasing frequency. Also the relative increase in the value of capacitance (from capacitance at 0 V to the maximum capacitance attained during forward biasing) is significantly smaller for higher frequencies. The capacitive response of the device to the applied bias is relatively low for higher frequencies. On addition of salt to the device, the absolute value of capacitance is higher for a given frequency and a given applied bias. More the amount of salt added to the polymer, more is the capacitance. Figures 10(a)–10(c) show the measured C - V curves for PLEDs with different amount

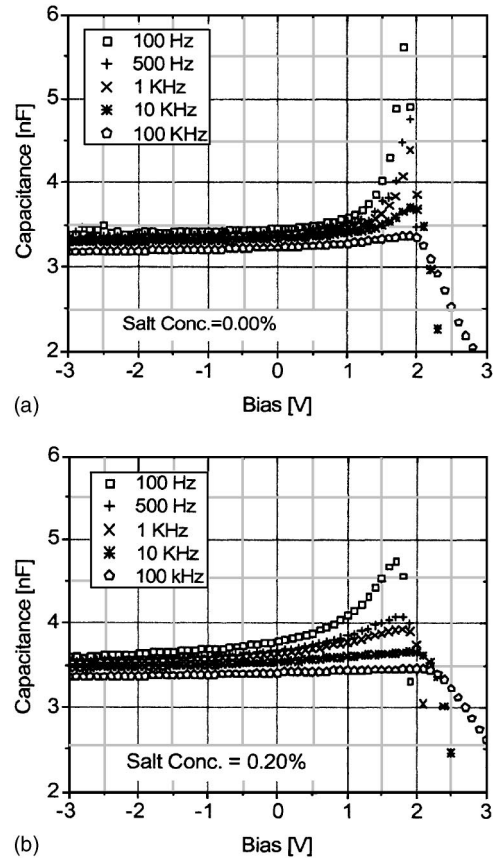


FIG. 9. Capacitance as a function of voltage and frequency for two different kinds of devices: (a) salt conc.=0.00 wt. %, and (b) salt conc.=0.20 wt. % of MEH-PPV.

of salt added to the polymer at frequencies 100 Hz, 10 kHz, and 1 MHz, respectively. From the figure it can be observed that the geometric capacitance C_0 is 2.8 nF for the device with no added salt and increases to 8.1 nF for device with 1 wt. % added salt. This increase in zero-bias capacitance is because of two reasons: one, the salt LiCF_3SO_3 has a higher dielectric constant than MEH-PPV; and two, more initial charged defects are present near the interface in the polymer layer because of ionic electrolyte. The junction capacitance depends on the amount of charge density according to $C \propto \sqrt{N_d}$.²⁰ This gives the increase in the capacitance of about 3.1 times on increasing the salt concentration from 0.1 wt. % to 1.0 wt. %, which is close to the value of 2.9 ($=8.1/2.8$) as measured. On the other hand, the amount of injected charge present in the polymer after majority charge injection is lesser in the polymer layer which contains added salt, as some of the charge is trapped and recombined. This results in smaller increase in the value of capacitance after majority charge injection bias for the devices with added salt as compared to the device without any salt.

IV. CONCLUSION

In conclusion, we have demonstrated that the onset voltages of increase and decrease the capacitance of a typical PLED correspond to the majority and minority charge-injection voltage under forward biased condition. Also the relative increase in the capacitance of the device depends on

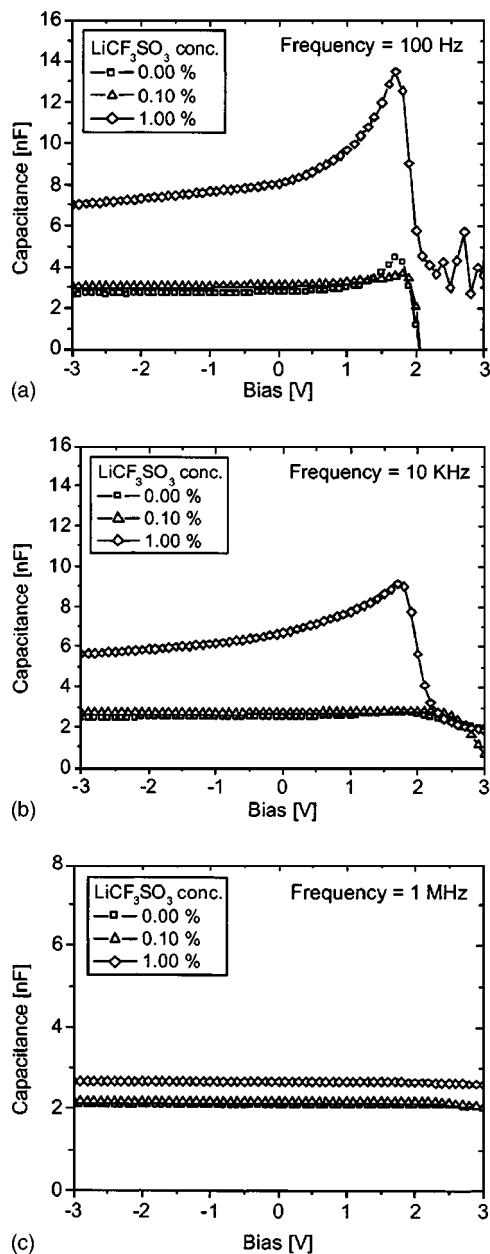


FIG. 10. Capacitance as a function of voltage for PLEDs with different salt concentration for frequencies of (a) 100 Hz, (b) 10 kHz, and (c) 1 MHz.

the amount of charge injected into the polymer layer, which in turn depends on the work function of the cathode. Also, the ionic impurities play an important role in determining the device characteristics and the device performance of the PLEDs. Although it is well known that the salt ions that are

present in the polymer layer will worsen the performance of the PLED, not much is known about the behavior and mechanisms that these ions play in the polymer. In order to study the effect of ionic impurities in PLEDs, we have made an attempt to study the effect of ions by going in a backward direction, i.e., by adding salt to initially pure polymer. We discussed the effect of addition of salt into the polymer with the help of various characterization techniques such as I - V characteristics, luminescence measurements, ac impedance measurements, and C - V measurements.

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