Impedance Spectroscopy of
π-Conjugated Organic Materials

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AC electrical properties of organic light-emitting diodes with poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV), poly[2,5-bia(dimethyloctylsilyl)-1,4-phenylene-vinylene] (BDMOS-PPV), and tris-(8-hydroxyquinolate)-aluminum (AlQ$_3$) as light-emitting materials are studied. The frequency-dependent real and imaginary parts of impedance were fitted using an equivalent circuit. We found that the conduction mechanism is a space-charge limited current with exponential trap distribution.

Keywords: Organic, Semiconductor, impedance, spectroscopy.

I. Introduction

The organic light-emitting diode (OLED) and polymeric light-emitting diode (PLED) are two of the most promising candidates for use in future flat panel displays [1]-[3]. Recently, the organic or polymer electroluminescence (EL) device has been widely reviewed and studied [4]. However, only a few experimental results from electrical impedance studies of polymer EL and polymer light-emitting electrochemical cells (LECs) have been reported thus far [5]-[9]. Extensive electrical information on OLED and PLED devices such as charge transport and charge injection mechanisms can be obtained from an impedance study. This is because transport of the charge carriers at direct current or at very low frequencies requires a kind of percolation network of transition, in which the weakest links (intra-chain connection) determine the magnitude of the conductivity. At higher frequencies, the charge carriers become localized in small regions of low-energy barriers [9].

The electrical impedance of polymer EL employing poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) was first measured by Campbell, and others. [5]. They used thin transparent gold as the positive contact and calcium as the negative contact. According to their experimental results, a capacitance increase due to the charging of the traps was observed under a small forward bias, while a capacitance decrease, due to the neutralization of the traps, was observed under a large forward bias. The real and imaginary parts of the impedance were fitted using the equivalent circuit of a parallel capacitor and parallel resistor network with a series resistor which comes from the ohmic contact between the polymer and the metal electrode.

The capacitance-voltage (C-V) and current-voltage (I-V) measurements of the polymer LECs were also performed by

Campbell, and others, and the results were compared with the steady-state device model calculation [6]. They revealed that the electrochemical junction began to form prior to a significant current flow. Yu, and others [7], measured the complex admittance of polymer LECs and proposed a novel operating scheme which separately controls the distribution of ionic charges and the flow of electronic currents. The combination of a slow ionic response and a rapid electronic response made possible the use of a pulsed driving scheme in which the peak value independently controls the carrier injection. Despite these efforts, however, an understanding of the electrical properties in polymer EL devices is not yet complete.

In this study, therefore, we investigate the ac electrical response of three kinds of OLEDs and PLEDs with poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV), poly[2,5-bia(dimethyloctylsilyl)-1,4-phenylene-vinylene] (BDMOS-PPV), and tris-(8-hydroxyquinolate)-aluminum (AlQ₃) as light-emitting materials. Frequency-dependent impedance data are obtained in the range of 10^{-2} Hz to 10^{7} Hz, and the devices are modeled with the equivalent circuits. From the equivalent circuit analysis, conducting mechanisms and dielectric behaviors of those three π-conjugated light-emitting materials are discussed.

II. Experimental Procedures

Details of the light-emitting diode fabrication are described in [10]. Polymer (MEH-PPV and BDMOS-PPV) films were obtained by spin coating the filtered polymer solution onto the substrates with indium-tin-oxide (ITO) electrodes, which were pre-cleaned by successive ultrasonic treatment for an hour in acetone and isopropyl alcohol, followed by a drying period using nitrogen gas, and then dried in a vacuum oven for several hours. AlQ₃ was purchased from TCI Co. and purified by sublimation. AlQ₃ was deposited at a rate of 2 to 3.5 Å/s. Aluminum, which was vapor deposited, was used as a cathode at a working pressure below 4×10^{-6} Torr, yielding an active size of 4 mm².

The thicknesses of the MEH-PPV, BDMOS-PPV, and AlQ₃ films are 35 nm, 40 nm, and 100 nm, respectively. The impedances of the samples are measured using an impedance gain/phase analyzer (SI1260, Solatron) and dielectric interface (SI2690, Solatron) in the frequency range of 10^{-2} Hz to 10^{7} Hz.

III. Results and Discussions

Figures 1(a), (b), and (c) show the current-voltage (I-V) curves of the devices using MEH-PPV, BDMOS-PPV, and AlQ₃, respectively. At low voltage, the currents increase linearly with a voltage increase for all three samples which
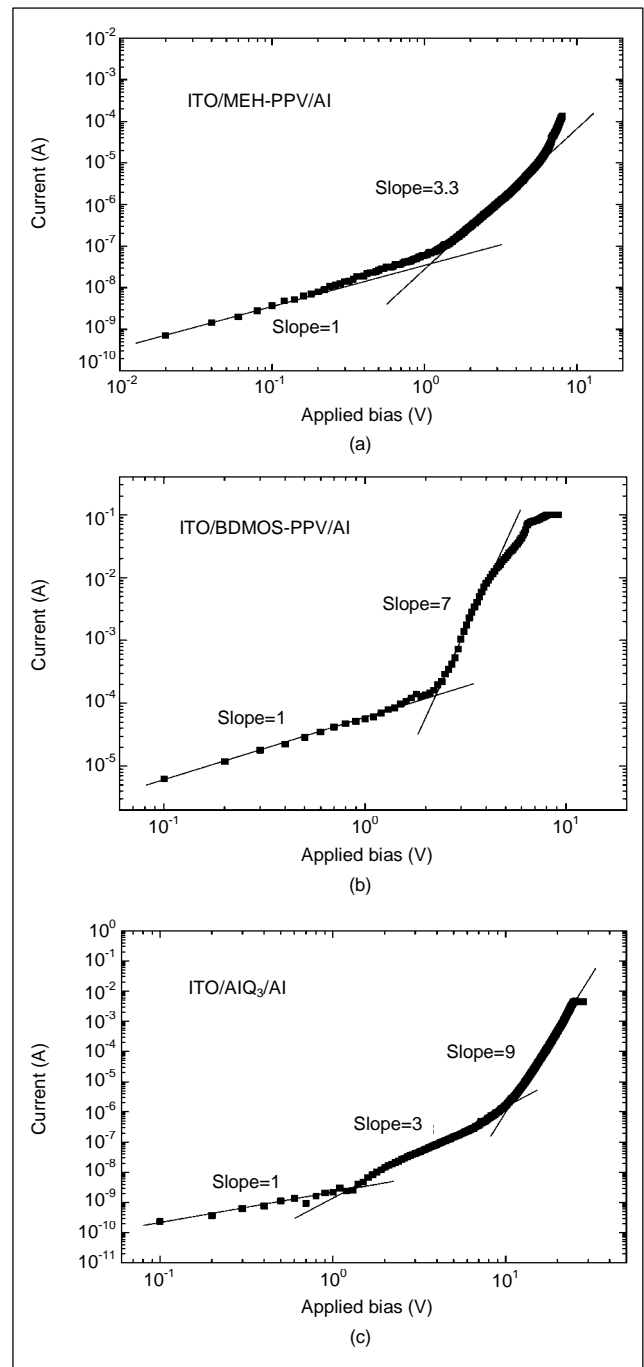

Fig. 1. I-V characteristics of the (a) ITO/MEH-PPV/Al, (b) ITO/BDMOS-PPV/Al, and (c) ITO/AlQ₃/Al devices. The current is ohmic at low voltages, while at higher voltages the current is bulk limited.

means that the I-V characteristics are ohmic. This indicates that no schottky barriers were formed between the ITO/organic and organic/Al interfaces. At higher voltages, the current increases no more linearly. From the space-charge-limited current (SCLC) with an exponential trap distribution theory, a voltage-dependent current for a one-carrier dominated transport, "hole" in this case, is given by

$$J = \frac{KV^{m+1}}{d^{2m+1}}, \qquad (1)$$

where d and K are the thickness of the film and the proportional constant, respectively The slopes of 3.3 and 7 in the log I-log V graphs, as shown in Figs 1(a) and (b), represent the exponent m and become 2.3 and 6 for MEH-PPV and BDMOS-PPV, re-
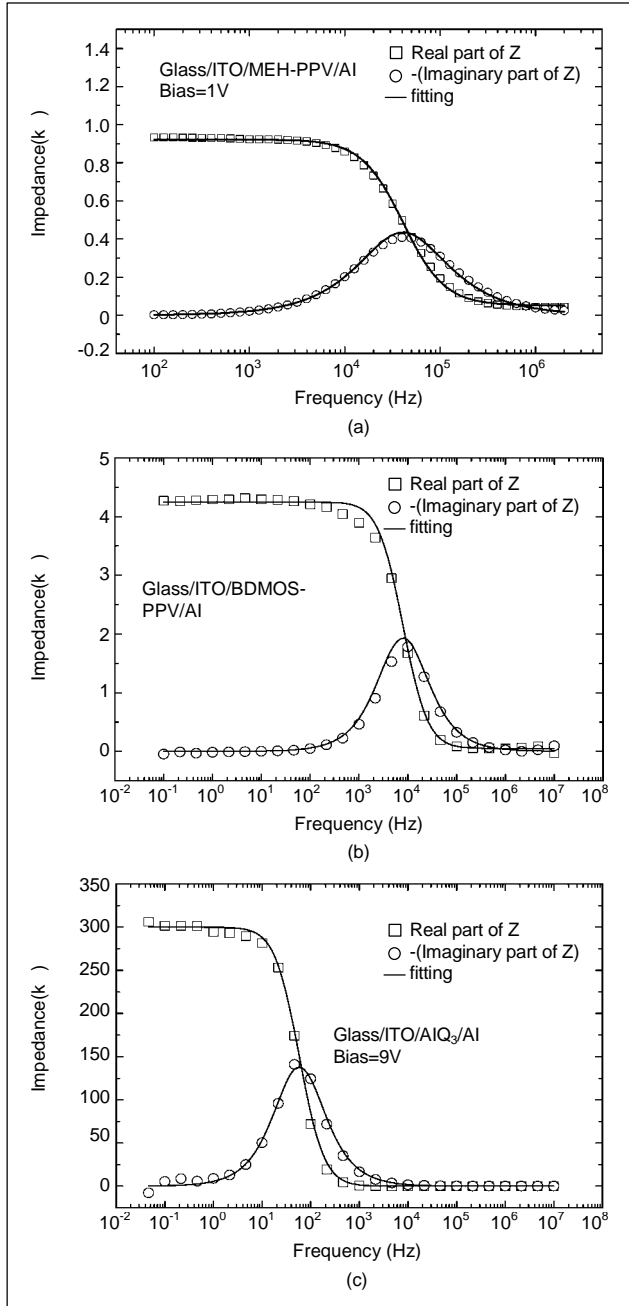

Fig. 2. The frequency-dependent real and imaginary parts of the impedance of the (a) ITO/MEH-PPV/Al, (b) ITO/ BDMOS-PPV/Al, and (c) ITO/AlQ$_3$/Al devices. Symbols are measured data and the solid lines are the fitting data using the equivalent circuit.

spectively. In the case of AlQ$_3$, the slopes in the bulk limited region change from 3 to 9. Therefore, the parameters m for the devices are 2 and 8. These two parameters show that there are two kinds of trap states exponentially distributed in the sample within a given applied bias voltage.

Figure 2 shows the frequency-dependent real and imaginary parts of the impedances of the (a) ITO/MEH-PPV/Al, (b) ITO/BDMOS-PPV/Al, and (c) ITO/AlQ$_3$/Al devices. Symbols indicate the measured data, while the solid lines indicate the fitting data using the equivalent circuit of a single parallel resistor R$_p$ and capacitor C$_p$ network with serial resistor R$_s$, as shown in Fig. 3. The capacitor C$_p$ represents the capacitive component of the device, and parallel resistor R$_p$ is for the leakage current running through the device. The serial resistor R$_s$ represents the contact resistance among the organic semiconductor, ITO and Al electrodes, and lead wires.
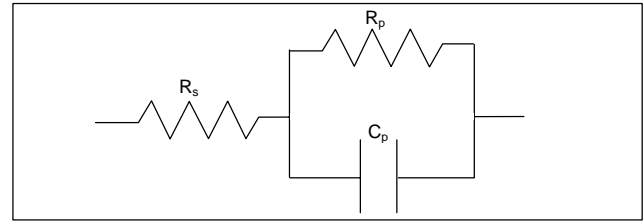

Fig. 3. Equivalent circuit of single parallel resistor R$_p$ and a capacitor C$_p$ network with a serial resistor R$_s$ for the devices.

According to this equivalent circuit analysis, there is no interfacial capacitance, or if one exists it is negligibly small. This suggests that there are negligible insulating barriers, such as oxides like Al$_2$O$_3$, or air gaps formed between the polymer and the top and bottom electrodes. The data are well fitted for all devices within the measured frequency ranges.

The variations of the fitting parameters according to the applied bias voltages are shown in Figs. 4 (a), (b), and (c) for ITO/MEH-PPV/Al, ITO/BDMOS-PPV/Al, and ITO/AlQ$_3$ devices, respectively. The R$_p$ decreases as the dc bias voltage increases, while the C$_p$ is almost independent of bias voltage for all the devices. From (1), the voltage dependence of R$_p$ is given by

$$R_P \propto \frac{V}{J} \propto V^{-m}. \qquad (2)$$

If the conduction mechanism is the SCLC with exponential trap distribution, according to (2), R$_p$ should decrease linearly in a log R$_p$ vs. log V plot with a slope of –m. The plot of log R$_p$ vs. log V is shown in the inset in Fig. 4 (a) for the ITO/MEH-PPV/Al device, and the value of m is about 2.6, indicated by the linear fitting of the data. The linear dependence of log R$_p$ vs. log V implies that the conductance of the hole in the MEH-PPV film follows the SCLC with exponential trap distribution.
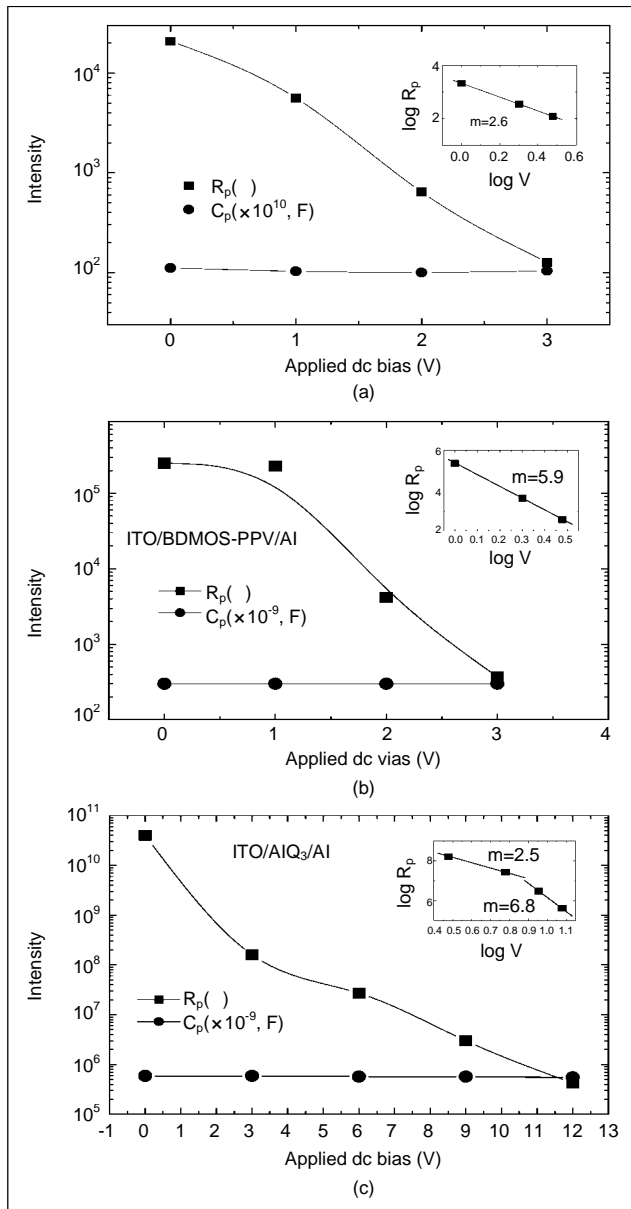
Fig. 4. The variation of the fitting parameters of (a) ITO/MEH-PPV/Al, (b) ITO/BDMOS-PPV/Al, and (c) ITO/AlQ$_3$ devices using the equivalent circuit of a single parallel resistor R$_p$ and a capacitor C$_p$ network with serial resistor R$_s$. The insets show the plot of log R$_p$ vs. log V.

The carriers may be trapped by chemical impurities and/or structural defects. Meanwhile, C$_p$ is independent of the applied bias. In the case of LECs, the capacitance increased at high-bias voltages due to the forming of an electrochemical junction caused by the mobile ions [6], [7]. The capacitance increased at low-frequencies, as shown in [7], due to these mobile ions, while no capacitance increase was observed in this study because there are no mobile ions in LEDs. The invariance of C$_p$ with applied bias is exactly the behavior expected for the SCLC conditions, where the C$_p$ calculated for an SCLC with exponential trap

distribution is given by C$_p$ =[(2m+1)ε$_r$ε$_o$A]/[d(m+1)] [10]. We think that the configurational and chemical structure of the MEH-PPV does not change due to the applied voltage.

As shown in Figs. 4(b) and (c), the results are similar with that of the ITO/MEH-PPV/Al device. For the device using BDMOS-PPV, we obtained a value of 5.9 for the exponent m using a linear fitting of the parameter R$_p$ in the log V vs. log R$_p$ plot, and which, as shown in Fig. 1(b) is almost the same as the value of 6 obtained using an I-V measurement—the slope value of 7 is derived from m+1 as presented in (1). For the AlQ$_3$ device, as shown in Fig. 4(c), the exponent m changes from 2.5 to 6.8 when increasing the bias voltage from 10 V to 12 V. These values are also similar with those obtained from the I-V measurement shown in Fig. 1(c). From these results, we can conclude that the conduction mechanism of all three organic materials used in these experiments is an SCLC with exponential trap distribution.

According to the previous report [9], the conduction mechanism of the ITO/MEH-PPV/Al device was studied using a generalized Langevin equation. Also, according to the results of the previous report, the conduction mechanism of the device is an SCLC with exponential trap distribution and an exponent m of 2.46. Therefore, all three kinds of analysis, I-V plot, equivalent circuit analysis, and generalized Langevin analysis, indicate simultaneously that the charge conduction mechanism of the ITO/MEH-PPV/Al device is an SCLC with exponential trap distribution and an exponent m of 2.46 within fitting error.

From the SCLC theory, the total charge trap density can be calculated. The current density J in an SCLC with exponential trap distribution theory is given by

$$J = N_c \mu q^{1-m} \left[\frac{\varepsilon_r m}{N_t (m+1)} \right]^m \left(\frac{2m+1}{m+1} \right)^{m+1} \frac{V^{m+1}}{d^{2m+1}}, \qquad (3)$$

where the total trap density, N$_t$, is calculated as $6.6{\times}10^{19}$/cm^3 using N$_c \sim 10^{20}$/cm^3 [11], [12], $\mu{=}8.5{\times}10^{-6}$ cm^2/Vs [13], $\varepsilon_r{=}4$, d=100 nm, and m=2.46. In polymeric materials, there are two kinds of charge carriers, hole (electron) and ion(s). We used home made MEH-PPV, and because some ionic materials were used for the synthesis of MEH-PPV, such as K$_+$ for polymerization and Na$_+$ for monomer synthesis, some traces of these elements might remain even after several purification steps are taken. Therefore, the traps could be either hole traps or ion traps. However, the charge carrier traps, as we mentioned above, are probably mainly hole traps because the majority of charge carriers were revealed as holes [8]. Unlike holes, ions (when present) cannot penetrate the electrode and are accumulated while they undergo a hopping process. Therefore, if an external field is applied, hopping ions move toward the electrode and are accumulated while the external field exists.

This accumulated charge behaves as additional capacitance and affects the low-frequency real part of the dielectric constant [14]. One thing we have to remember is that this effect does not alter the frequency-dependent imaginary part of dielectric constant because the accumulated charges are static. This effect is well known as either the "Maxwell-Wagner effect" or "the transport limitation at the boundary." The additional capacitance, which is frequency-dependent due to the accumulation charge, can be written as $C \sim \kappa\omega^{-1}$. However, we did not observe any sign of additional capacitance in our previous work [9]. This strongly suggests that the charge carrier is not of the ion type, but is rather a hole carrier.

We obtained the dielectric constants for the three materials used from the equation $C_p=[(2m+1)\varepsilon_r\varepsilon_o A]/[d(m+1)]$, which can be calculated for an SCLC with exponential trap distribution [11]. The calculated values are 3.8, 5.7, and 6.7 for MEH-PPV, BDMOS-PPV, and AlQ_3, respectively.

IV. Summary

AC electrical properties of organic light-emitting diodes (OLEDs) with MEH-PPV, BDMOS-PPV, and AlQ_3 as light-emitting materials were studied. The frequency-dependent real and imaginary parts of impedance were fitted onto the devices using an equivalent circuit with a single parallel resistor R_p and a capacitor C_p network with a series resistor R_s. The conduction mechanism of the π-conjugated materials used in this study is a space-charge-limited current with exponential trap distribution. The exponents m for the MEH-PPV and BDMOS-PPV are 2.6 and 5.9, respectively, and the two exponents of 2.5 and 6.8 were observed for the AlQ_3 device. The total trap density of the MEH-PPV device was calculated as $6.6\times10^{19}/cm^3$.

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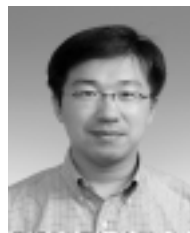
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