Electrical characterization studies and doping effects of rubidium carbonate in organic layer by admittance spectroscopy

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A B S T R A C T

The doping effects and electrical characteristics of rubidium carbonate (Rb_2CO_3) in organic bipolar charge transport material 2-methyl-9,10-di(2-naphthyl) anthracene (MADN) has been investigated. Utilizing temperature-dependent admittance spectroscopy, the electron injection barrier (so-called activation energy) is verified to be reduced from 1.33 to 0.2878 eV by the incorporation of Rb_2CO_3 from 0 to 33 vol%. The precision of admittance spectroscopy is further proved by photovoltaic measurement. Higher mobility has achieved using space-charge-limited current (SCLC) determination. Consequently, these enhancements in electron injection and transport yield superior device performance for organic light-emitting diodes (OLEDs).

1. Introduction

In regard to achieve highly efficient organic electroluminescent devices, high driving voltage and low power efficiency are fatal issues from a practical point of view [1–3]. For the past decades, a large part of work in this field has taken the advantage of electrical doping of inorganic compounds, atoms or molecules to improve the intrinsic insufficiency of organic materials on conductivity and charge injection ability [4–9]. By doping electron accepting (p-type) or donating (n-type) dopants into an organic material, one could successfully tune the Fermi level (E_F) toward the transport energy states, ending up facilitating carrier injection and reducing Ohmic losses [10–13]. Particularly, for an OLED, it is more desirable and crucial to find suitable candidates for electron injection due to the inherently unbalanced carrier mobility of holes and electrons under identical applied electric field [14]. Correspondingly, it is also critically indispensable to have an intensive understanding of the electric characteristics and physical mechanisms based on these dopant-host systems. Among all the reported methodologies, admittance spectroscopy (AS) and impedance spectroscopy (IS) are powerful techniques to elucidate the dynamics and electric properties of electrically doped organic layers [15–19]. With appropriate equivalent circuit model, each separated layer in a multilayered organic device can be considered as a unit composed of a capacitance (C) and a resistance (R) in parallel, which exhibits independent resistance-capacitance (RC) property [16,18,21].

Consequently, material characteristics such as activation energy, carrier concentration and carrier mobility can be directly determined by AS analysis [18,19,22]. In addition, unlike other alternatives such as ultraviolent photoemission spectroscopy (UPS), inverse photoemission spectroscopy (IPES) and time-of-flight (TOF), AS imposes no specific environment requirements (e.g., ultra-high vacuum), which is more compatible with the realistic device operating and fabrication conditions [20,23].

MADN has been utilized as a host material for fluorescent emitters [24,25] and transport material for both holes and electrons [26,27] owing to its wide band gap and bipolar charge transport property [with hole and electron mobilities of $(2–4) \times 10^{-7}$ cm^2/Vs] [24]. Additionally, MADN processes stable chemical characteristics and is hard to react with lithium fluoride, which can avoid chemical device degradation [28]. Since the first studies of a Li doping for OLED cathode interfaces proposed in 1990s [29], alkali metal compounds have been common n-type dopants for electron transporting layers (ETLs), such as cesium fluoride (CsF) [30], sodium carbonate (Na_2CO_3) [31] and cesium carbonate (Cs_2CO_3) [32]. Rubidium-based salts were also demonstrated as effective n-type dopant or buffer material (e.g., RbF [33] and $RbNO_3$ [34]) which can decrease the Ohmic loss at the interface between the ETL and cathode. Rubidium carbonate (Rb_2CO_3) has been demonstrated by Park et al. in 2013 as an effective n-type dopant in Alq_3 organic matrix [35]. Diverse OLED applications such as inverted bottom emission OLEDs has also employed Rb_2CO_3 doped films on

indium tin oxide (ITO) cathode as electron injection layer [36]. Regarding to different chemical processes occur during the doping, it has been shown that the properties of these alkali-doped organic films would be quite differing while using various dopant-host combinations [35,37]. However, the improvement of electron injection ability for these published rubidium-based materials was usually explained only with UPS, x-ray photoemission spectra (XPS) [35,36]. It would be beneficial to investigate their doping effects with other measurements like AS and IS which provide in-depth physical information for further mechanism understandings.

In this paper, we investigated the doping effects of a newly proposed n-type electron injection layer, which consists of rubidium carbonate doped MADN. The electrical characteristics of MADN:Rb_2CO_3 were studied by temperature-dependent admittance spectroscopy, photovoltaic and charge-space-limited current and measurements. In view of that, the electrical property enhancements were contributed to the improved device performance of OLEDs. The results obtained from typical Alq_3-based OLEDs in this study could be employed to other emission systems such as phosphorescence and thermally activated delayed fluorescence (TADF) based OLEDs.

2. Experimental details

All the devices used in this work were fabricated on patterned ITO/glass substrates (with sheet resistance of $15\,\Omega$/square) by thermal evaporation at a base pressure of 1×10^{-6} Torr. Prior to the deposition, the substrates should go through a series of cleaning procedure, then undergo a 20-minute UV-ozone treatment. The layers composed of MADN:Rb_2CO_3 with various doping concentrations were accomplished by co-evaporation from two independent evaporating sources. The active area of devices was 2.5×2.5 mm^2 defined by the overlap of ITO and Al cathode. Deposition rates of different materials were monitored by quartz crystal thickness monitors. Current density-voltage-luminance (*J-V-L*) measurements were carried out under room temperature with a computer-controlled system integrated with a power source (Keithley-2400) and a spectrophotometer (Photo Research PR-655). AS analysis was perceived by Agilent 4294A precision impedance analyzer at a frequency range of 40 Hz to 10 MHz with oscillation signal of 50 mV. UPS measurement was performed with a photoelectron spectrometer (Riken Keiki, model AC-2). The UV–visible absorption spectra were acquired by a spectrophotometer (HITACHI U-3310).

3. Results and discussion

Fig. 1 shows the electroluminescent (EL) characteristics of five OLEDs in a configuration of ITO/NPB (40 nm)/Alq_3 (40 nm)/Rb_2CO_3:MADN (5 nm, x%)/LiF (1 nm)/Al (120 nm), where NPB [N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine] was used as a hole transport material, Alq_3 [Tris-(8-hydroxyquinoline)aluminum] was used as both green fluorescent emitter and electron transport layer, and the Rb_2CO_3 doped MADN was served as an electron injection layer (EIL). In the EILs, the Rb_2CO_3 doping concentration was varied in a range of volume percentage from 0% to 33% (0%, 15%, 20%, 25% and 33%, respectively). As shown in Fig. 1(a) and (b), by increasing the dopant concentration, the driving voltage is reduced and the luminance is dramatically increased. For example, the operating voltage decreases from 5.4 to 5.3, 5.1, 4.2 and 4.7 V at the luminance of 100 cd/m^2 by applying concentration 15%, 20%, 25% and 33% compared to device with pristine MADN (0%). On the other hand, the maximum luminance of devices with a doping percentage of 15%, 20%, 25% and 33% is 18,462, 20,952, 26,694, 22,673 cd/m^2 respectively, compared to 15,530 for the pure MADN device. This result is a great indicator of electron injection and transport enhancements attributed to the doping of Rb_2CO_3.

The current efficiency versus current density properties are shown in Fig. 1(c). Significant improvements in luminance efficiency can be
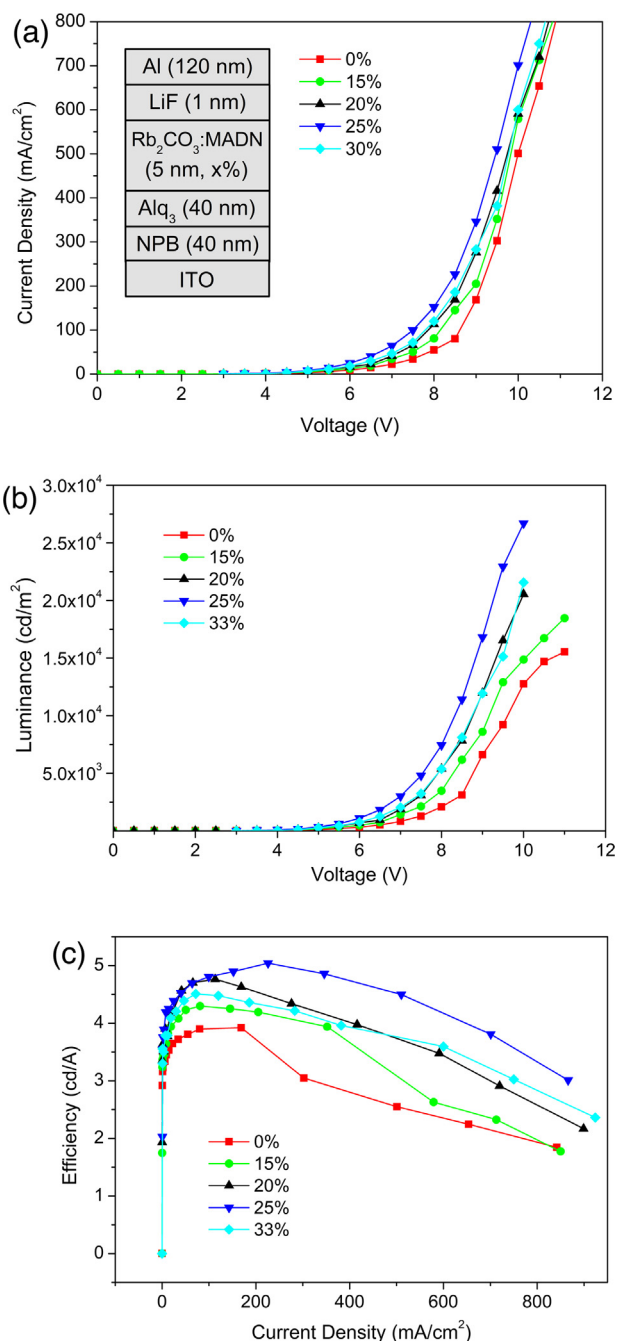

Fig. 1. (a) *J-V*, (b) *L-V* and (c) *E-J* characteristics of OLEDs with ITO/NPB (40 nm)/Alq_3 (40 nm) /Rb_2CO_3:MADN (5 nm)/LiF (1 nm)/Al(120 nm), where the doping concentration of Rb_2CO_3 varies from 0 to 33%.

observed. The efficiency intensely enhanced by employed the Rb_2CO_3 dopant. The device with 25% MADN:Rb_2CO_3 exhibits a maximum current efficiency of 5.1 cd/A, while devices with doping concentration of 0%, 15%, 20%, 33% present 3.9, 4.3, 4.8, 4.5 cd/A, respectively. The detailed EL characteristics are summarized in Table 1. The result in Fig. 1 indicates the integration of Rb_2CO_3 into MADN can significantly improve the electrical characteristics of OLEDs, which is highly comparable to its alkali counterparts [29–32]. It is worth noting that further increase of the dopant concentration to 33% leads to a degeneration of EL performances, both in driving voltage and current efficiency. It has been demonstrated that the alkali ion in a highly doped organic layer may act as luminescence quencher while it immigrates into the emission layer, also ending up with defect generation [38]. The similar