



Effects of incorporating salts with various alkyl chain lengths on carrier balance of light-emitting electrochemical cells



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ARTICLE INFO

Article history:

Received 18 April 2014

Received in revised form 15 August 2014

Accepted 15 August 2014

Available online 28 August 2014

Keywords:

Light-emitting electrochemical cells

Salts

Carrier balance

ABSTRACT

Recently, solid-state light-emitting electrochemical cells (LECs) have attracted much attention since they have advantages such as low operation voltages, simple device structure and balanced carrier injection. Salts are commonly added in the emissive layer of LECs to provide additional mobile ions and thus to accelerate device response. However, in addition to modified ionic property, carrier balance of LECs would also be tailored by salt additives. In this work, we improve device efficiency of LECs by incorporating imidazole-based salts bearing various alkyl chain lengths. As the alkyl chain length of the added salt increases, the device current decreases and the recombination zone approaches the anode. These results reveal that hole transport in the emissive layer of LEC containing a salt with a larger size would be impeded more significantly than electron transport. When doped with a salt possessing a proper size, nearly doubled device efficiency as compared to that of the neat-film device can be obtained due to improved carrier balance. This work demonstrates a feasible strategy to improve device performance of LECs and clarifies the physical insights of the effect of salt size on carrier balance of LECs.

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1. Introduction

As compared to conventional organic light-emitting diodes (OLEDs), which have been shown to exhibit great potential in displays and solid-state lighting, solid-state light-emitting electrochemical cells (LECs) possess several further advantages. In the emissive layer of LECs, electrochemically doped regions induced by spatially separated mobile ions under a bias form ohmic contacts with electrodes, giving balanced carrier injection, low operating voltages and consequently high power efficiencies [1,2]. Hence, only a single emissive layer, which can be easily processed from solutions, is generally required in LECs. In addition, air-stable electrodes, e.g. Au and Ag can be used in LECs due to facilitated carrier injection by doped regions

while OLEDs typically require more sophisticated multi-layer structures and low-work-function cathodes [3]. The emissive-layer materials of LECs can be categorized into two types: conjugated polymers and cationic transition metal complexes (CTMCs). Polymer LECs are usually composed of an emissive conjugated polymer, a salt and an ion-conducting polymer to avoid phase separation [1,2]. However, for LECs based on CTMCs, no ion-conducting material is needed since these metal complexes are intrinsically ionic. Furthermore, higher electroluminescent (EL) efficiencies are expected due to the phosphorescent nature of the metal complexes. Owing to these advantages, LECs based on CTMCs have attracted much attention in recent years [4–26]. Efficient blue [20,23], green [9,14], yellow [11] and white-emitting [25] CTMC-based LECs have been reported to show high external quantum efficiencies (EQEs) >10%.

Ionic salts have been commonly added in the emissive layer of LECs to improve device performance [27–29].

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Additional mobile ions provided by the salt additives can reduce the time required for the formation of the doped layers, fastening the device response [27–29]. Furthermore, the device efficiencies of polymer LECs were shown to be dependent on the cation size of the added salts [30]. The emission zone position in the emissive layer of planar polymer LECs have also been shown to be related to the cation size of the added salts [30]. A recent literature depicted that interfacial packing of salt cations at the cathode of CTMC-based LECs enhances electron injection efficiency, resulting in more balanced hole and electron concentrations [29]. These results indicate that the salt additives not only affect the ionic mobility and doping propagation speed but also alter the carrier balance of LECs. To optimize device efficiencies of LECs, overall carrier balance including carrier injection and transport should be considered. However, few reports concerning detailed effects of varying the molecular size of the added salts on carrier balance of sandwich LECs have been published [30,31]. In this work, several imidazole-based salts containing various alkyl chain lengths are incorporated in the emissive layer of CTMC-based LECs and their device characteristics are compared. The device current monotonically decreases as the alkyl chain length of the salt increases since a larger salt molecule increases the intermolecular distance between the emissive complexes and impedes carrier transport. In spite of decreased device current, the device efficiency in the LECs doped with salts is improved as compared to the neat-film devices. The trend of device efficiency versus the alkyl chain length of the salt corresponds to the recombination zone position in the LEC device. More centered recombination zone in the emissive layer suffers less degree of exciton quenching and leads to a higher device efficiency consequently. These results demonstrate a feasible way to optimize the carrier balance of LECs by doping a salt with a proper alkyl chain length.

2. Experiment section

2.1. Materials

The host complex (**1**) used in the emissive layer of the LECs was Ru(dtb-bpy)₃(PF₆)₂ (where dtb-bpy is 4,4'-diterbutyl-2,2'-bipyridine) [5]. Complex **1** was purchased from Luminescence Technology. The salts used in this study were 1-ethyl-3-methylimidazolium hexafluorophosphate (EMIMPF₆), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIMPF₆) and 1-octyl-3-methylimidazolium hexafluorophosphate (OMIMPF₆). OMIMPF₆ was purchased from Tokyo Chemical Industry and the other salts were purchased from Alfa Aesar. All materials were used as received.

2.2. LEC device fabrication and characterization

Indium tin oxide (ITO)-coated glass substrates were cleaned and treated with UV/ozone prior to use. A thin poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) layer (30 nm) was spin-coated at 4000 rpm onto the ITO substrate in air and was then baked at

150 °C for 30 min. For the thinner devices (**N1**, **E1**, **B1**, **H1** and **O1**), the emissive layers were then spin-coated at 3000 rpm from the acetonitrile solutions of complex **1** or complex **1** and salts (80 mg mL⁻¹). The emissive layer of the device **N1** was composed of a neat film of complex **1** while those of the devices **E1**, **B1**, **H1** and **O1** contained complex **1** doped with EMIMPF₆, BMIMPF₆, HMIMPF₆ and OMIMPF₆, respectively (molar ratio of complex **1** and salt = 2.1: 1). For the thicker devices (**N2**, **E2**, **B2**, **H2** and **O2**), the concentrations of the solutions used for spin coating of the emissive layers were 250 mg mL⁻¹. The rotation speed for spin coating and the components of the emissive layers of the thicker devices were the same with those used for their thinner counterparts. The thicknesses of the thinner and thicker devices were measured by ellipsometry to be ca. 250 and 600 nm, respectively. After spin coating of the emissive layers, the samples were then baked at 70 °C for 10 h in a nitrogen glove box, followed by thermal evaporation of a 100-nm Ag top contact in a vacuum chamber (~10⁻⁶ torr). The electrical and emission characteristics of LEC devices were measured using a source-measurement unit and a calibrated Si photodiode. All device measurements were performed under constant bias voltages in a nitrogen glove box. The EL spectra were taken with a calibrated CCD spectrograph.

3. Results and discussions

The molecular structures of the salts used in this study are shown in Fig. 1. The alkyl chain length increases in the order; EMIMPF₆, BMIMPF₆, HMIMPF₆ and OMIMPF₆. The physical properties of the salts used in this study are summarized in Table 1. The volume per molecule of each salt was calculated from the molar mass and density data [32–34]. The molecular volume of the salt increases with the alkyl chain length since a longer alkyl chain occupies more space. When doped in the emissive layer of LECs, the salt molecules tend to increase the intermolecular distance between the emissive complexes. As shown in Fig. 2,

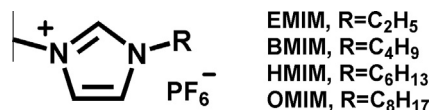


Fig. 1. Molecular structures of the salts used in this study.

Table 1
Summary of the physical properties of the salts used in this study.

Salt	Molar mass (g mol ⁻¹)	Density (g cm ⁻³) ^a	Volume per molecule (nm ³) ^b
EMIMPF ₆	256.13	1.56 ^c	0.274
BMIMPF ₆	284.18	1.37 ^d	0.346
HMIMPF ₆	312.24	1.29 ^e	0.403
OMIMPF ₆	340.29	1.24 ^d	0.457

^a At 298 K.

^b Calculated from molar mass and density data.

^c Ref. [31].

^d Ref. [32].

^e Ref. [33].

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